

D R A F T

EVALUATION OF HYDROCARBON REACTIVITIES
FOR USE IN CONTROL STRATEGIES

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ABSTRACT

A combined experimental and chemical computer modeling research program has been carried out to develop and evaluate an experimental protocol for the determination of organic reactivities.

While it is well recognized that organics emitted into the atmosphere have a wide range of reactivities, the precise definition and ranking of organic reactivities is still a matter of debate, and in fact depends on the actual physical and chemical environment considered. Moreover, because of the recently recognized influence of chamber-dependent radical initiation processes on the gas phase chemistry of irradiated NO_x -organic-air mixtures, data obtained from single NO_x -organic-air systems are of only qualitative value. Thus, we have employed the irradiation of NO_x -multicomponent organic-air mixtures to which incremental additions or deletions of the test organic were made.

Based upon a previous SAPRC/ARB 13-component surrogate hydrocarbon mixture designed to account for organic emissions from all sources into the South Coast Air Basin, we first developed a 4-component surrogate mixture (the "mini-surrogate") which mimicked the more complex mixture in terms of maximum O_3 yields, NO oxidation rates and organic consumption rates. In all subsequent NO_x -organic-air irradiations incremental additions or deletions of the test organic were made to this 4-component mini-surrogate mixture. Irradiations were carried out under either dual-mode (in a 40,000 liter outdoor all-Teflon chamber) or single-mode (in a 6400 liter indoor all-Teflon chamber) conditions. The majority of the irradiations were carried out under single-mode conditions, and the effects of addition (or in some cases removal) of toluene, benzaldehyde, propene, n-butane, trans-2-butene, methanol, ethanol, and t-butyl methyl ether were determined in consecutive single-mode indoor chamber irradiations. In this series the standard mini-surrogate- NO_x run was alternated with runs with added or removed test organics.

As an integral part of this overall program, chemical kinetic computer modeling studies were also carried out using the most up-to-date kinetic and mechanistic data. Within the experimental uncertainties, the data from the chamber irradiations were in agreement with the computer predictions. Of particular interest was the observation that, with respect to maximum O_3 yields, negative reactivities were observed for toluene and benzaldehyde, (i.e., the maximum O_3 concentrations were reduced in the presence of these two organics), while propene and trans-2-butene exhibited slightly negative or zero reactivities under the particular experimental conditions employed. However, in terms of NO oxidation, all of the organics studied, apart from benzaldehyde, enhanced the oxidation rates.

The chemical reasons for these observed effects are interpreted in terms of our current knowledge of the atmospheric chemistry of the organics studied, and the relevance of this research program to the development of emission control strategies by the CARB is discussed.

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I. PROJECT SUMMARY

In this report a project is described which was designed to develop and evaluate protocols for the determination of selected aspects of the reactivities of organic air pollutants.

It is well recognized that the organic compounds emitted into the atmosphere from mobile and stationary sources have a wide range of reactivities (Altshuller and Bufalini 1971 and references therein, Dimitriades 1974, Darnall et al. 1976a, Pitts et al. 1976a,b). However, the precise definition and ranking of organic reactivities has been a subject of debate (see, for example, Pitts et al. 1976a,b, 1978, Farley 1978, Cox et al. 1980) and, in fact, any such ranking of organics almost certainly depends on the physical and chemical environment considered. A number of reactivity criteria have been used in the past, such as organic consumption rates, NO to NO₂ conversion rates, ozone yields, ozone dosage, eye irritation, and reactivity towards the hydroxyl (OH) radical (Altshuller and Bufalini 1971, Heuss and Glasson 1968, Glasson and Tuesday 1970a, 1971, Darnall et al. 1976a, Pitts et al. 1976a,b, 1978). However, as may be expected, the organic reactivity rankings derived from these differing criteria are not, in general, the same.

With the advent of rules requiring emissions trade-offs for new sources and the continuing need for cost-effective control strategies, a combined experimental and chemical computer modeling investigation concerning the utility of protocols for the determination of relative organic reactivities is of considerable interest to the California Air Resources Board and other regulatory agencies. Clearly, such an investigation must involve conditions and reactivity criteria which are relevant to ambient atmospheric conditions found in California's urban areas. Thus, of the criteria previously proposed or used, the most appropriate appear to be the maximum yields of ozone and the initial rates of NO oxidation and O₃ formation.

Previous studies dealing with the ozone-forming potential of organics (e.g., Wilson and Doyle 1970, Glasson and Tuesday 1970b, Laity et al. 1973) have generally employed NO_x-air irradiations of a single organic in each experiment. However, recent studies in these laboratories concerning the occurrence and quantification of chamber-dependent radical sources

(Carter et al. 1981, 1982a, Pitts et al. 1981, 1983) have shown that the data obtained from such single NO_x-organic-air systems may be of no more than qualitative or semi-quantitative value when used to derive organic reactivities (Pitts et al. 1978).

In order to minimize chamber effects associated with the single organic systems, in this program a multi-hydrocarbon-NO_x-air system has been used, to which the organics being studied were added incrementally. Hydrocarbon reactivity was then considered in terms of the limiting incremental reactivity, I_R^0 , which, for the purpose of this program, is defined as follows:

$$I_R^0 = \lim_{\Delta[\text{organic}] \rightarrow 0} \left(\frac{R^{\Delta[\text{organic}]} - R^0}{\Delta[\text{organic}]} \right) \quad (I)$$

where R refers to a given measure of reactivity (e.g., maximum O₃ yields, NO oxidation rates, average radical levels, etc.), R⁰ is the reactivity measurement obtained in a standard multi-hydrocarbon-NO_x-air environmental chamber experiment, and R^{Δ[organic]} is the corresponding reactivity measurement observed when the initial concentration of the organic of interest has been changed by an amount Δ[organic]. I_R^0 thus reflects the effects of adding small amounts of an organic compound to mixtures designed to represent polluted atmospheres. This approach is advantageous because it (a) minimizes chamber effects on the gas phase chemistry since only small changes in the chemistry generally occur from run to run, and (b) more closely simulates the introduction of an organic into a polluted urban atmosphere.

The overall goal of this program has therefore been to measure the incremental reactivities of selected representative organic compounds of interest to the California Air Resources Board, and in general to investigate the utility and implications of this concept of reactivity. The general approach employed is briefly summarized as follows:

a) A simplified four- or five-component hydrocarbon mixture was developed to represent the complex mixture of organics emitted into urban atmospheres. A multi-component organic mixture which represents emissions of organics from all sources in the South Coast Air Basin has been

previously developed and used at the Statewide Air Pollution Research Center (SAPRC) (Pitts et al. 1976c,d, 1980). The development of the four- or five-component surrogate mixture (hereafter referred to as the mini-surrogate) required comparisons of the data from NO_x -air photooxidations of the SAPRC 13-component mixture with those of various potential mini-surrogate mixtures until good agreement was obtained. In particular, the mini-surrogate mixture was considered to be a good representation of the full 13-component system when the NO_x -air irradiations of the two mixtures gave agreement within $\sim \pm 20\%$ for various reactivity parameters (e.g., ozone formation rate, maximum ozone yields, and overall radical levels as measured by hydrocarbon disappearance rates). The composition of the mini-surrogate mixture which satisfied these criteria, given in Table I-1, was used as the basis of the incremental reactivity studies which constituted the bulk of this program.

b) An initial series of irradiations of NO_x -mini-surrogate-air irradiations, with incremental additions of toluene, were carried out to test the overall experimental approach. Two types of experiments were carried out: (i) Dual-mode irradiations using an outdoor $\sim 40,000$ liter all-Teflon chamber with the mini-surrogate mixture in one side and the mini-surrogate mixture plus an incremental addition of toluene in the other. These dual-mode chamber irradiations allowed a control irradiation to be carried out at the same time under identical conditions. (ii) Single-mode NO_x -mini-surrogate-air irradiations interdispersed among NO_x -mini-surrogate + toluene-air irradiations using the ~ 6400 liter indoor all-Teflon chamber. These initial experiments were successful in that

Table I-1. Composition of the Mini-Surrogate Mixture Derived and Employed in this Program

Organic	Mole %
n-Butane	72.7
Propene	17.3
m-Xylene	7.3
trans-2-Butene	2.6

measurable effects of incremental additions of toluene were observed, namely suppression of the O_3 maximum yield and enhancement of the initial rates of NO oxidation and O_3 formation. The results from the two different experimental approaches were reasonably consistent with each other. The dual-mode approach was judged to be more precise because the irradiation of the control and the test mixtures could be conducted at the same time under the exact same experimental conditions. However, it was concluded that the single-mode approach was more appropriate for routine use since it was found (at least for toluene) to give results which are consistent with results of dual-mode experiments, was experimentally easier and less costly to employ, and could be done under more reproducible conditions than outdoor dual-mode experiments, allowing for more reliable inter-compound comparisons.

c) In view of these considerations, the major portion of the experimental program involved a series of single-mode NO_x -mini-surrogate-air irradiations interdispersed among irradiations of the same mixture with incremental additions of toluene, benzaldehyde, ethanol, t-butyl methyl ether, and methanol, or with incremental additions or deletions of the mini-surrogate components propene, n-butane, and trans-2-butene. Chamber characterization runs [NO_x -air irradiations with added trace amounts of organic tracers (Carter et al. 1982a) and actinometry measurements] were also interdispersed between the NO_x -organic-air irradiations in order to maintain a continuous record of chamber effects and light intensities for these irradiations.

d) Concurrently with this experimental program, chemical kinetic computer modeling was carried out to determine whether the observed changes in reactivity due to the incremental additions of the organic being studied were consistent with the current understanding of the chemistry occurring in these organic- NO_x -air irradiations, and to evaluate the dependence of the change in reactivity on the amount of the organic added. To this end, the organics used in the surrogate hydrocarbon mixture and those incrementally added to this surrogate mixture were chosen to be those for which present chemical knowledge is sufficient for chemical computer modeling to be of use.

The incremental reactivity parameters observed in this second series of indoor Teflon chamber irradiations and those derived from chemical

kinetic model calculations simulating these irradiations are summarized in Table I-2, where the uncertainties given for the experimental values reflect the variability of the replicate NO_x -mini-surrogate-air irradiations. From Table I-2 it can be seen that some of the calculated values of the incremental reactivity parameters fall outside the range of the estimated experimental uncertainties. Furthermore, except for toluene, the calculated suppression of the average hydroxyl radical levels, $\langle \text{OH} \rangle$, by these organics was consistently less than that derived from the experimental rate. However, the results of the model calculations were qualitatively consistent with the experimental data in terms of the overall ordering of reactivity by the various criteria, and with the observation of "negative" reactivities for certain compounds. Thus, in general, the results of the experiments are reasonably consistent with the current understanding of the kinetics and mechanisms of organic- NO_x -air irradiations.

Although there are difficulties in precisely measuring incremental reactivity values for relatively unreactive compounds such as methanol, in general it can be concluded that the experimental technique employed in this program can be used successfully for a wide range of organics. For the majority of the compounds studied in this program the incremental reactivities, defined in terms of the maximum O_3 yields and the NO oxidation rates, were measured with sufficient precision to allow meaningful comparison with theoretical values derived from computer model calculations. The agreement was sufficiently good to indicate that there were no significant experimental problems or artifacts. For the most reactive compounds, such as benzaldehyde, trans-2-butene, and propene, the effects were large enough so that the dependence of the measured incremental reactivities (i.e., $\Delta[\text{reactivity}]/\Delta[\text{organic}]$) on the amounts of test compound added to the mini-surrogate ($\Delta[\text{organic}]$) could be determined. These results were also reasonably consistent with the model calculations.

For the less reactive compounds, such as methanol, ethanol, t-butyl methyl ether, and n-butane, the dependence of the incremental reactivity on the amount of test compound added could not be determined with any precision. For those compounds, however, the model calculations indicated that this dependence is small. This suggests that, at least for these

Table I-2. Summary of Observed and Calculated Limiting Incremental Reactivities for the Eight Organics Studied in this Program

Compound ^a	I _{max} ^o . O ₃		I _A ^o ([O ₃]-[NO])/Δt ^b (10 ⁻³ min ⁻¹)		I _{<OH>} ^c (10 ⁶ cm ⁻³ ppm ⁻¹)	
	Obs	Calc	Obs	Calc	Obs	Calc
Methanol	0.01 ± 0.02	0.014	0.1 ± 0.4	0.25	0.01 ± 0.15	-0.03
t-Butyl methyl ether	0.028 ± 0.011	$\begin{Bmatrix} 0.069 \\ 0.038 \end{Bmatrix}^d$	0.4 ± 0.3	$\begin{Bmatrix} 1.12 \\ -0.42 \end{Bmatrix}^d$	-0.34 ± 0.05	$\begin{Bmatrix} -0.13 \\ -0.28 \end{Bmatrix}^d$
n-Butane	0.06 ± 0.01	0.056	0.8 ± 0.1	0.42	-1.00 ± 0.01	-0.37
Ethanol	0.01 ± 0.02	0.024	0.8 ± 0.3	0.47	-0.52 ± 0.09	-0.27
Toluene	-0.28 ± 0.13	-0.067	2.3 ± 1.5	2.47	-0.3 ± 0.2	-1.6
Benzaldehyde	-1.0 ± 0.3	-0.77	-12 ± 3	-34.6	-9 ± 2	-4.7
Propene	0.12 ± 0.05	0.175	5.6 ± 0.9	11.1	-3.1 ± 0.2	-1.23
trans-2-Butene	0.2 ± 0.3	-0.16	44 ± 6	48.3	-4.0 ± 0.8	-3.5

^aListed in order of increasing OH radical rate constant.

^bAverages of the values for t = 0-15 min and t = 15-45 min.

^cCalculated from the amounts of m-xylene consumed during the irradiations (see Section IV.C).

^dTop value is calculated assuming no alkyl nitrate formation from this reaction of NO with the peroxy radicals formed from TBME; bottom value is calculated assuming 20% alkyl nitrate formation. See Section IV.D.

compounds, experiments in which sufficiently large amounts of test compound are added to allow a measureable effect to be observed will probably give reasonable estimates of the incremental reactivity values when only small amounts of the compound are added.

The experiments conducted in this program allowed a ranking of the reactivities of the eight organics studied to be made. However, the data obtained clearly indicated that the rankings would differ depending on how reactivity is defined. In addition, the data indicated that some compounds, including those which are quite reactive when irradiated by themselves in NO_x -air mixtures, exhibit negative reactivity in terms of maximum O_3 yields. Benzaldehyde exhibited by far the largest negative reactivity by all criteria, being the only compound we studied which was unambiguously negatively reactive in terms of NO oxidation rates as well as O_3 yields. This was not unexpected, since benzaldehyde is known to be an efficient radical inhibitor. However, toluene was the next most negatively reactive of the compounds studied in terms of O_3 yields, and propene and trans-2-butene were either slightly negative or slightly positive. All three of these compounds were highly reactive in terms of O_3 formation when irradiated in single hydrocarbon- NO_x -air mixtures (see, for example, Pitts et al. 1979), and had positive incremental reactivity when defined in terms of NO oxidation rates. Indeed, the alkenes had the highest measured and calculated incremental reactivities relative to NO oxidation rates of all the compounds studied. The remaining compounds studied exhibited positive incremental reactivities both in terms of O_3 yields and NO oxidation rates, with the ordering of the reactivities being approximately what one would expect based on the rates of their reactions with the OH radical.

As indicated above, the observed incremental reactivities, including the "negative" reactivity effects discussed above, were reasonably consistent with the results of model calculations, which means that these effects can be accounted for in terms of the current understanding of the atmospheric transformation mechanisms of the compounds studied. In particular, the low or negative incremental reactivity with respect to maximum O_3 yields, observed for compounds which are highly reactive by themselves and which had a positive incremental reactivity relative to NO oxidation rates, can be explained by the presence of significant NO_x -

removal pathways in the photooxidation of these compounds. This causes O_3 formation to cease (due to lack of NO_x) earlier than would be the case if the compound were not present in the mixture. For toluene, this effect was large enough to more than counter the effect of its inducing more rapid O_3 production when NO_x is present. For the alkenes, the two opposing effects tended to cancel each other, thus causing a relatively small net effect on the O_3 yields, despite their relatively high rates of reaction in NO_x -air systems.

Another general conclusion which can be drawn from the results of this study is that, for most compounds, the effect on final O_3 yields of adding organics to NO_x -air mixtures already containing other organics (e.g., polluted urban atmospheres) is relatively small. Specifically, the addition of test compounds resulting in a 25% increase of the total ppmC of organics present in the mixture caused, in all cases except for benzaldehyde (which as indicated above had a very large and negative effect), less than a 10% change in the maximum O_3 . This is consistent with most EKMA-type analyses (e.g., Singh et al. 1981, Carter et al. 1982b, and references therein), which predict that large percentage reductions in hydrocarbons are required to significantly reduce O_3 levels.

The implication of the results of this study in terms of deriving reactivity scales for emission control strategy purposes are unfortunately difficult to assess. The existence of compounds, such as benzaldehyde, which tend to suppress all aspects of photochemical smog related to O_3 formation and transformation rates has been recognized for some time (Gitchell et al. 1974). Obviously control decisions regarding such compounds must be based on other criteria, such as potential formation of toxic products or enhanced aerosol formation. The situation is less obvious, however, for compounds which are highly reactive by most measurements but which tend to suppress, or at least not significantly enhance, O_3 yields when added to already polluted mixtures. Even if one is concerned only with ozone levels, and neglects other important considerations such as formation of toxic products or aerosols, it does not appear to be advisable to consider compounds such as toluene to be less reactive than compounds such as ethanol or n-butane, simply on the basis of their incremental effects on O_3 levels. In particular, under conditions where NO_x is in excess (which was not the case for the experiments reported

here), the tendency of toluene to remove NO_x from the system, which causes reduced O_3 levels in NO_x -poor systems, will not be important, and ozone levels will then be more strongly influenced by the rate at which O_3 is formed. Thus toluene would be expected to have a positive incremental reactivity with respect to O_3 formation under these conditions.

Perhaps the most important conclusion that can be drawn from this study is that, even if one is concerned only with O_3 formation, it is a gross over-simplification to attempt to define a single reactivity scale for organics, where a given order of ranking represents the O_3 -forming potential of a compound under all conditions. Thus, further research in this direction would probably not be useful. A more profitable approach would be to derive multi-parameter reactivity scales, where each parameter represents a different aspect of the atmospheric chemistry of the various organics (such as overall reaction rates, tendencies to suppress or enhance radical and NO_x levels, NO oxidation efficiencies, etc.). This approach would then involve the development of techniques, probably based on computer modeling, to use these parameters to calculate the effects of increasing or reducing emissions of organics of interest under the conditions of a specific source area. This obviously will be a difficult approach to implement, since it requires a fairly complete knowledge of the levels of reactive compounds present in the source area as well as extensive research programs concerning the various reactivity characteristics of organics, and how best to measure them and employ them in control strategy calculations.

Progress is being made in this regard as our knowledge of the atmospheric photooxidation mechanisms of a large number of classes of organics, and of the identities and levels of the species present in polluted air basins, improve. Progress is also being made on the development of more reliable and sophisticated techniques to model the transformations occurring in such air basins. However, it will be a number of years before reliable techniques are developed to derive hydrocarbon reactivity scales appropriate for the various source areas of concern. Clearly, until such techniques are available, existing hydrocarbon reactivity scales should be used only with great caution in making emission control strategy decisions.

II. INTRODUCTION AND BACKGROUND

It is well recognized that the organic compounds emitted into the atmosphere from mobile and stationary sources have a wide range of reactivities (Altshuller and Bufalini 1971 and references therein, Dimitriadis 1974, Darnall et al. 1976a, Pitts et al. 1976a,b). However, the precise definition and ranking of organic reactivities has been a subject of debate (see, for example, Pitts et al. 1976a,b, 1978, Farley 1978, Cox et al. 1980) and, in fact, any such ranking of organics almost certainly depends on the physical and chemical environment considered. A number of reactivity criteria have been used in the past, such as organic consumption rates, NO to NO₂ conversion rates, ozone yields, ozone dosage, eye irritation, and reactivity towards the hydroxyl (OH) radical (Altshuller and Bufalini 1971, Heuss and Glasson 1968, Glasson and Tuesday 1970a, 1971, Darnall et al. 1976a, Pitts et al. 1976a,b, 1978). However, as expected, the organic reactivity rankings derived from these differing criteria are not, in general, the same.

With the advent of rules requiring emissions trade-offs for new sources and the continuing need for cost-effective control strategies, a combined experimental and chemical computer modeling investigation into the utility of protocols for the determination of relative organic reactivities is of great interest to the California Air Resources Board and other regulatory agencies. Such an investigation into reactivity protocols should obviously involve conditions and reactivity criteria which are relevant to ambient atmospheric conditions found in California's urban areas. Thus, of the criteria previously proposed or used, the most appropriate appear to be maximum yields of ozone and initial rates of NO oxidation and O₃ formation.

Previous studies dealing with the ozone-forming potential of organics (e.g., Wilson and Doyle 1970, Glasson and Tuesday 1970b, Laity et al. 1973) have generally employed NO_x-air irradiations of a single organic in each experiment. However, recent studies in these laboratories concerning the occurrence and quantification of chamber-dependent radical sources (Carter et al. 1981, 1982a, Pitts et al. 1981, 1983) show that the data obtained from single NO_x-organic-air systems may be of no more than qualitative or semi-quantitative value when used to derive organic reactivities

(Pitts et al. 1978a). This will be particularly true for organics of low reactivity towards the OH radical (i.e., organics which react slowly in NO_x-organic-air systems) or which have radical sinks in their NO_x-air photooxidation chemistry. For such organics the chamber radical source becomes the major supplier of radicals, overwhelming the radical flux from the gas-phase NO_x-organic-air chemistry, and the system then becomes "chamber driven."

In this program, in order to minimize such chamber effects associated with the single organic systems, we have employed a multi-hydrocarbon-NO_x-air system to which the organics to be studied were added incrementally. Hydrocarbon reactivity has then been considered in terms of the incremental reactivity, $I_R^{\Delta[\text{organic}]}$, which for the purpose of this program is defined as follows:

$$I_R^{\Delta[\text{organic}]} = \frac{R^{\Delta[\text{organic}]} - R^0}{\Delta[\text{organic}]} \quad (I)$$

where R refers to a given type of measurement of reactivity (e.g., maximum O₃ yields, NO oxidation rates, average radical levels, etc.), R⁰ is the reactivity measurement obtained in a standard multi-hydrocarbon-NO_x-air environmental chamber experiment designed to be reasonably representative of atmospheric conditions, and R^{Δ[organic]} is the corresponding reactivity measurement observed when the initial concentration of the organic of interest has been changed by an amount Δ[organic]. Since $I_R^{\Delta[\text{organic}]}$ will in general depend on Δ[organic], it is useful to remove this dependence by defining the limiting incremental reactivity, I_R^0 , as

$$I_R^0 = \lim_{\Delta[\text{organic}] \rightarrow 0} I_R^{\Delta[\text{organic}]} \quad (II)$$

for the purpose of comparing reactivities of different organics. This approach has the advantages that it (a) minimizes chamber effects on the gas phase chemistry since only small changes in the chemistry generally occur from run to run and (b) more closely simulates the introduction of an organic into a polluted urban atmosphere.

The overall goal of this program has therefore been to measure the incremental reactivities of selected representative organic compounds of interest to the California Air Resources Board, and in general to investigate the utility and implications of this concept of reactivity. The general approach employed is shown schematically in Figure II-1 and briefly summarized as follows:

a) A simplified four- or five-component hydrocarbon mixture was developed to represent the complex mixture of organics emitted into urban atmospheres. At the Statewide Air Pollution Research Center (SAPRC) we have previously (Pitts et al. 1976c,d) developed and used a multi-component organic mixture to represent emissions of organics from all sources in the Los Angeles Basin. This multi-organic mixture was subsequently

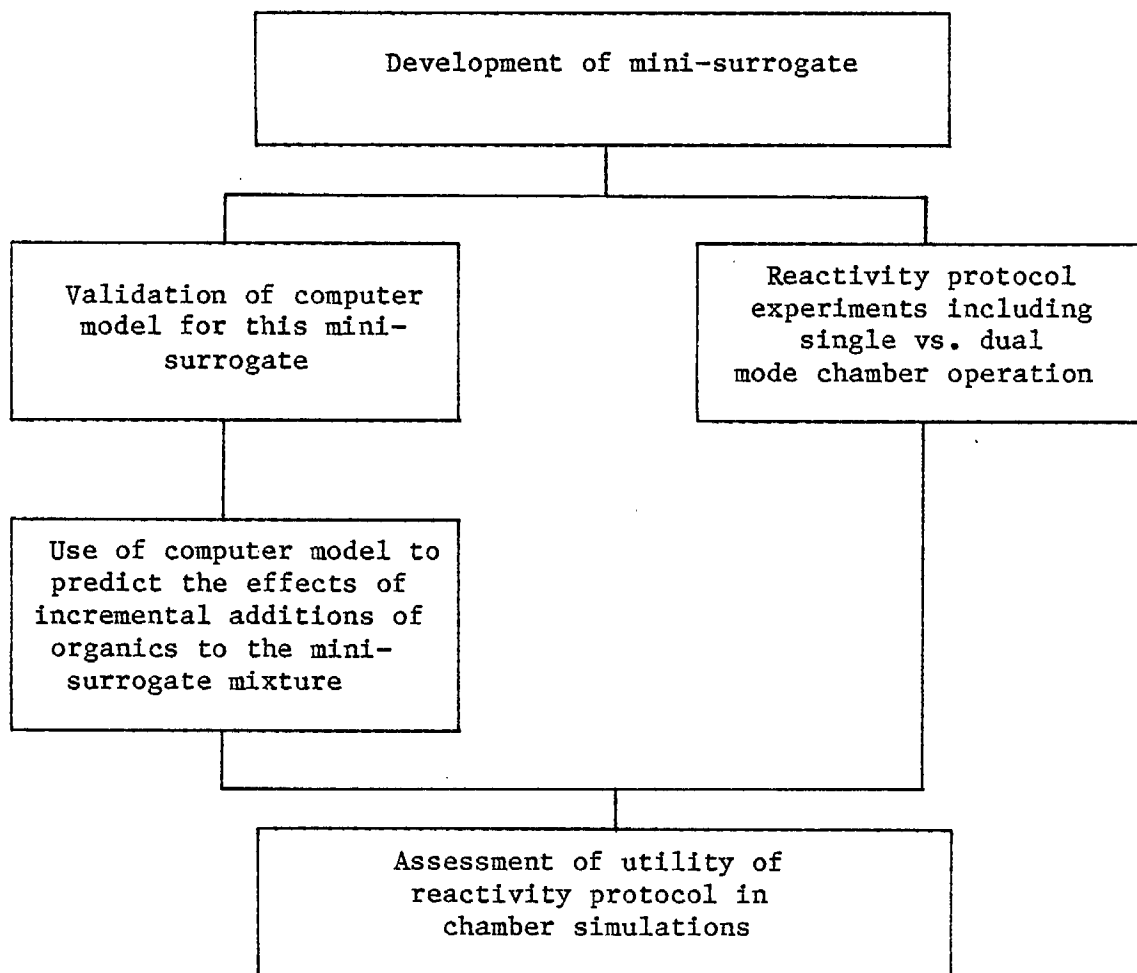


Figure II-1. Schematic of Technical Approach.

modified slightly to give a better representation of the different types of alkanes and to simplify the representation of the oxygenates (Pitts et al. 1980). This modified 13-part surrogate hydrocarbon mixture (Table II-1) was taken to be a reasonably satisfactory representation of organics emitted into urban atmospheres in California. The development of the four- or five-component surrogate mixture (hereafter referred to as the mini-surrogate) required NO_x -air photooxidations of the 13-component mixture shown in Table II-1 and of various potential mini-surrogate mixtures until the data from the mini-surrogate mixture were in good agreement with those for the 13-component mixture. The mini-surrogate mixture was considered to be a good representation of the full 13-component system. The NO_x -air irradiations of the two mixtures gave reasonably good agreement (within $\sim \pm 20\%$) between various reactivity parameters (e.g., the ozone formation rate, the maximum ozone yields and the overall radical levels as measured by hydrocarbon disappearance rates). The mini-surrogate mixture which satisfied these criteria was then used for the subsequent computer modeling and reactivity protocol experiments, as outlined below.

b) The major portion of the experimental program involved carrying out a series of irradiations of NO_x -mini-surrogate-air irradiations, with incremental additions or deletions (for the organic constituents of the mini-surrogate) of the organics to be studied. Two types of irradiation experiments were carried out. (i) Dual-mode chamber operation with the mini-surrogate mixture in one side and the mini-surrogate mixture plus an incremental addition of the organic being studied in the other. These dual-mode chamber irradiations allowed a control irradiation to be carried out at the same time under identical conditions. (ii) Single-mode chamber NO_x -mini-surrogate-air irradiations interdispersed among the NO_x -mini-surrogate (with added or deleted organic)-air irradiations. The majority of the irradiations carried out in this program were of this latter type. Chamber characterization [NO_x -air irradiations with added trace amounts of organic tracers (Carter et al. 1982a) and actinometry] runs were also interdispersed between the NO_x -organic-air irradiations in order to maintain a continuous record of chamber effects and light intensities for these irradiations.

c) Concurrently with this experimental program, chemical kinetic computer modeling was carried out to determine whether the observed

Table II-1. Composition of SAPRC-ARB Surrogate Hydrocarbon Mixture
(from Pitts et al. 1980)

Hydrocarbon	Mole %	% Carbon
<u>Alkanes</u> -- Total	<u>64.0</u>	<u>65.3</u>
Ethane	13.0	6.5
Propane	5.8	4.4
n-Butane	27.6	27.8
2,3-Dimethylbutane	9.3	14.1
n-Hexane	8.3	12.5
<u>Alkenes</u> -- Total	<u>13.3</u>	<u>10.1</u>
Ethene	6.8	3.4
Propene	1.9	1.4
cis-2-Butene	2.4	2.4
2-Methyl-2-Butene	2.2	2.8
<u>Aromatics</u> -- Total	<u>9.2</u>	<u>17.9</u>
Toluene	2.7	4.8
m-Xylene	6.5	13.1
<u>Alkynes</u>		
Acetylene	<u>8.2</u>	<u>4.1</u>
<u>Oxygenates</u>		
Acetaldehyde	<u>5.2</u>	<u>2.6</u>

changes in reactivity due to the incremental additions of the organic being studied were consistent with our current understanding of the chemistry occurring in these organic-NO_x-air irradiations, and to evaluate the dependence of the change in reactivity on the amount of the organic added. To this end, the organics used in the surrogate hydrocarbon mixture and those incrementally added to this surrogate mixture have been chosen to be those for which our present chemical knowledge is sufficient for chemical computer modeling to be useful.

The experimental techniques used, the data obtained, the computer modeling data and the overall discussion of this approach to the determination of organic reactivities and its ramifications for the California Air Resources Board are discussed in the following sections.

III. EXPERIMENTAL

The irradiations were carried out in two chambers, the SAPRC indoor ~6400 liter all-Teflon chamber and an outdoor ~40,000 liter all-Teflon chamber. These environmental chambers and the experimental techniques employed are described below.

6400 liter all-Teflon chamber. This chamber (Figure III-1) consisted of an ~6400 liter all-Teflon (FEP, 2 mil thickness) reaction bag fitted inside an aluminum frame of dimensions 8 ft x 8 ft x 4 ft. Irradiation was provided by two diametrically opposed banks of 40 Sylvania 40-W BL blacklamps, backed by arrays of Alzak-coated reflectors. The light intensity in the chamber was controlled by switching off sets of lights as previously described (Darnall et al. 1981), and the light intensities were monitored by measuring the rate of photolysis of NO_2 in N_2 using the quartz-tube continuous flow technique of Zafonte et al. (1977).

Before each experiment, the chamber was filled and emptied at least three times with purified air (Doyle et al. 1977) and then filled with purified air at the desired relative humidity (50% for all these irradiations). All gaseous reactants were injected using gas-tight, all-glass gas syringes and were flushed into the chamber by a stream of ultra-high purity N_2 . For liquid reactants, the desired amount of the liquid was injected using a precision micropipette into a ~1 liter Pyrex bulb, and the contents flushed into the chamber by a stream of ultra-high purity N_2 .

The protocol for the NO_x -mini-surrogate (or mini-surrogate with or without the organic studied)-air irradiations was as follows. After filling the chamber with purified air at the desired humidity, a background gas chromatographic (GC) analysis was carried out using the instruments described below. If (as was the normal occurrence) no contamination problems were observed, the reactants were injected into the chamber and two pre-irradiation GC analyses were carried out. Providing that no problems were apparent, a further $t=0$ sample for GC analysis was taken and the lights turned on ($t=0$). Samples for GC analyses were then taken, usually every hour, during the irradiations.

NO_x -air irradiations, with minor (~10 ppb) added amounts of two organic tracers (propene and n-butane for the runs reported here) were routinely carried out to determine the chamber radical source (see Carter

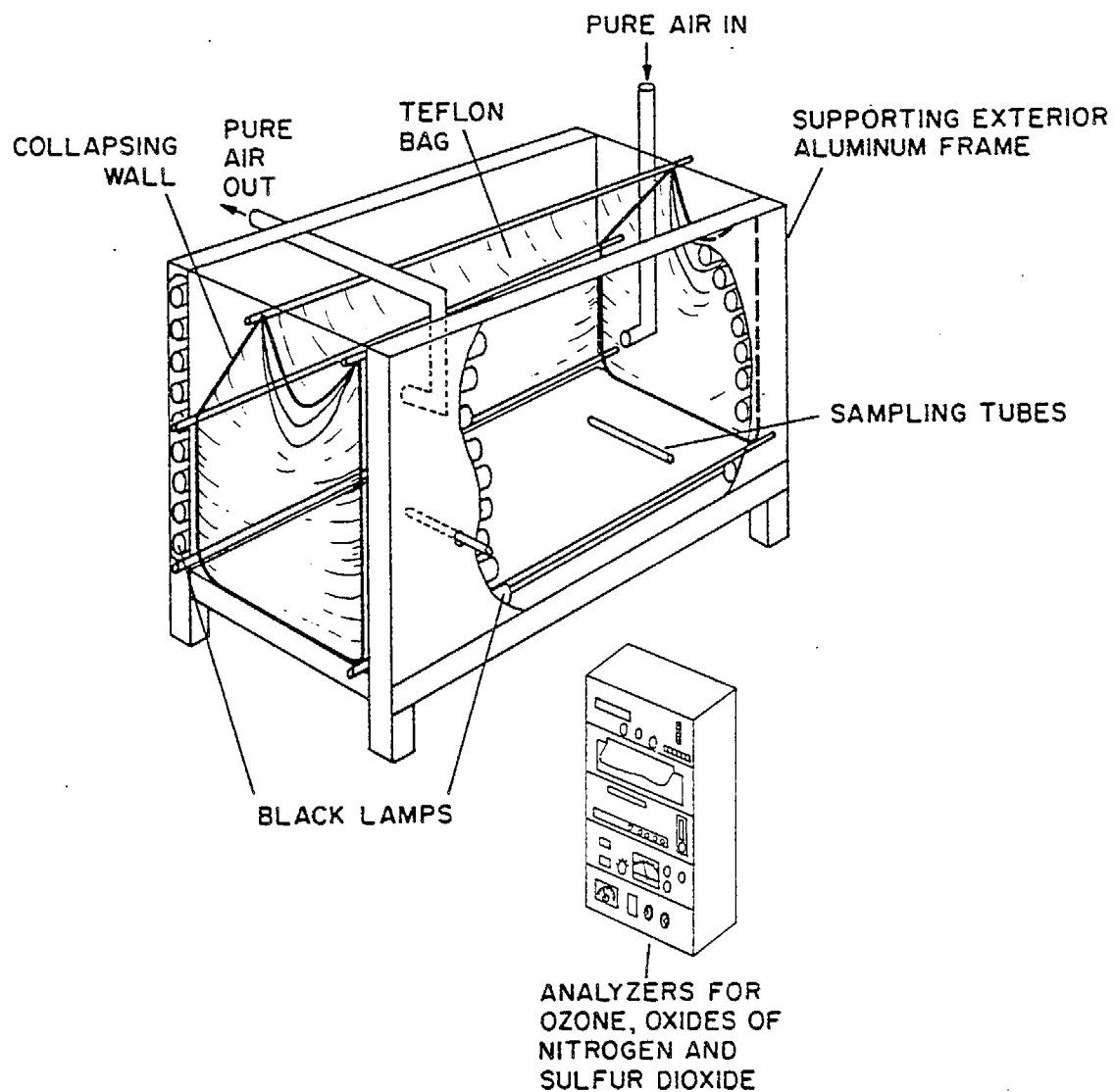


Figure III-1. SAPRC All-Teflon Indoor Chamber with Associated Analytical Data-Acquisition System.

et al. 1982a, Pitts et al. 1981, 1983, for a detailed discussion of this topic). These runs were primarily useful in providing the necessary chamber-dependent input data for chemical computer modeling, though they also provided data concerning the degree of contamination of the chamber. Actinometry experiments, as described below, were carried out with similar frequency (typically once every four NO_x -organic-air irradiations).

The 40,000 liter Dual-Mode Chamber. This 40,000 liter all-Teflon chamber was located outdoors, close to the SAPRC laboratories, and was used to carry out a series of NO_x -mini-surrogate-air irradiations with and without added toluene. For these experiments this chamber was used in the dual-mode configuration (Figure III-2) and irradiation was provided by natural sunlight. The analytical procedures were identical to those for the 6400 liter indoor chamber as described below. The major difference in the experimental procedures concerned the reactant injection technique. The chamber was filled with purified air at the desired humidity in the single-mode configuration and the NO_x and mini-surrogate injected into the chamber, still in the single-mode configuration. After mixing, the chamber was then divided by means of the pipes (Figure III-2) to dual-mode configuration, and the toluene added to one of the sides. During these filling and injection procedures, the chamber was covered, and after the pre- $t=0$ and $t=0$ analyses had been carried out as described above for the 6400 liter indoor all-Teflon chamber, the cover was removed and irradiation commenced. Gas chromatographic analyses were carried out once every hour during the irradiations.

When using this chamber in the dual-mode configuration, in essence a control irradiation was carried out under identical initial reactant concentrations (except for the incremental addition of the organic being studied) and physical parameters (e.g., temperature, solar radiation, etc.).

Analytical Techniques. The analytical techniques used were as follows. NO and NO_x were monitored by chemiluminescence analyzers and O_3 by ultraviolet absorption (Dasibi Model 1003AH). The O_3 analyzer was periodically calibrated by the California Air Resources Board, or calibrated, using the chamber, against an O_3 analyzer which had been so calibrated.

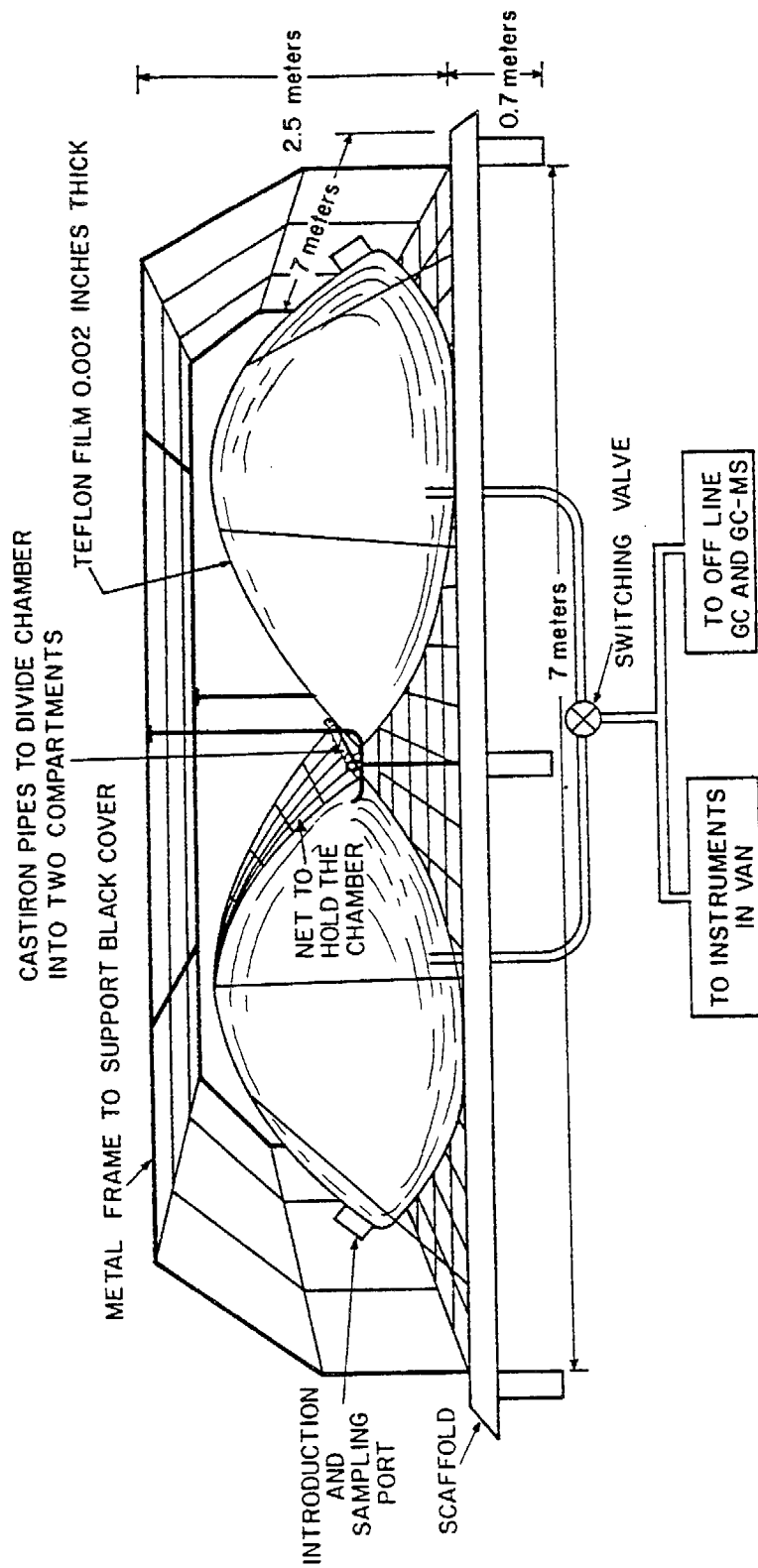


Figure III-2. SAPRC Outdoor Teflon Chamber Shown in Dual-Mode Configuration.

Acetaldehyde, acetone, ethanol, methyl ethyl ketone, 2-butyl nitrate, toluene, and m-xylene were quantitatively analyzed by gas chromatography with flame ionization detection (GC-FID) using a 10 ft x 0.125 in (o.d.) stainless steel packed column. The packing material consisted of 100% Carbowax 600, liquid phase, on a solid support of acid washed C-22 firebrick, 100/120 mesh. This column was maintained at 348 K throughout the entire chromatogram, with a nitrogen carrier flow of 50 mL min⁻¹. Increased sensitivity with the flame ionization detector was achieved by using oxygen instead of air, with the oxygen flow of 250 mL min⁻¹, and the detector heated to 433 K. The hydrogen flow was 45 mL min⁻¹. A 100 mL all-glass syringe was flushed three times with the contents of the Teflon chamber before the sample was taken. The sample was then "trapped" by flushing the 100 mL aliquot through a Valco gas sampling valve maintained at 368 K and through a 12 in x 0.125 in (o.d.) stainless steel, glass bead-packed trap immersed in liquid argon. The sample was thawed and transferred onto the GC column by simultaneously immersing the trap in boiling water and actuating the valve. The chromatogram was complete in ~12 minutes.

Propane, propene, isobutane, n-butane, acetylene, trans-2-butene, 2,3-dimethylbutane, n-hexane, cis-2-butene, and 2-methyl-2-butene were analyzed by GC-FID using a 34.5 ft x 0.125 in (o.d.) stainless steel packed column packed with a 10% liquid phase of dimethylsulfolane on a solid support of acid washed C-22 firebrick, 60/80 mesh. In series with this column was a 2 ft x 0.125 in (o.d.) stainless steel "soaker" column packed with 10% Carbowax 600 on acid washed firebrick, 30/60 mesh. These columns were maintained at 273 K by packing them in an ice-filled dewar. The detector temperature was 388 K. Both the nitrogen carrier gas and the hydrogen flows were 50 mL min⁻¹, and the oxygen flow was 300 mL min⁻¹. Sampling was performed by "trapping" a 100 mL sample on a 12 in x 0.125 in (o.d.) stainless steel trap packed with 10% dimethylsulfolane on firebrick immersed in liquid argon. The sample was thawed by removing the liquid argon, immersing the trap in ice water, and simultaneously switching the Valco gas sampling valve. The analysis required ~11 minutes for completion.

C₁ and C₂ hydrocarbons were monitored using a 5 ft x 0.125 in (o.d.) stainless steel column packed with Porapak N, 80/100 mesh. This column

was used isothermally at 333 K with a nitrogen carrier flow of 80 ml min⁻¹. The hydrogen and oxygen flows were 60 and 400 ml min⁻¹, respectively, and the flame ionization detector was heated to 333 K. Methane concentrations were determined by flushing a 2.0 ml stainless steel loop with a 100 ml sample, and transferring the 2.0 ml aliquot onto the column with a Valco gas sampling valve. Ethene, ethane, and acetylene concentrations were determined by trapping a 100 ml sample on a 11 in x 0.125 in (o.d.) 10% dimethylsulfolane on firebrick-packed trap immersed in liquid argon. The sample was transferred onto the column using an ice water thaw while switching the gas sampling valve. Methane chromatograms were complete in less than 1 minute, while ethene, ethane, and acetylene analyses required less than 2 minutes.

tert-Butyl methyl ether (TBME) was analyzed by GC-FID using a 20 ft x 0.125 in (o.d.) stainless steel column packed with liquid phases consisting of 2.5% Carbowax 20M and 2.5% DC-703 on a solid support of acid washed, dimethylchlorosilane-treated Chromosorb G, 100/120 mesh. The column was maintained isothermally at 333 K with a nitrogen carrier flow of 50 ml min⁻¹, and the flame ionization detector was heated to 493 K. The hydrogen flow was 45 ml min⁻¹, with the oxygen flow being 336 ml min⁻¹. Samples were analyzed by flushing a 3.0 ml stainless steel loop with 100 ml of sample, and then transferring the 3 ml sample onto the column using a Valco gas sampling valve. The chromatogram was complete in less than 4 minutes.

Benzaldehyde was monitored by GC-FID using a 5 ft x 0.125 in (o.d.) stainless steel column packed with 5% Carbowax 600 on acid washed firebrick, 100/120 mesh. The column oven was maintained at 363 K and the nitrogen carrier flow was set to 45 ml min⁻¹. The hydrogen and oxygen flows were 50 and 280 ml min⁻¹, respectively. Sampling was accomplished by flushing the 1 ml stainless steel loop with 100 ml of sample, and then transferring the 1 ml sample onto the column through a Valco gas sampling valve heated to 373 K. The analysis took approximately 9 minutes to complete.

Peroxyacetyl nitrate (PAN) was monitored using a gas chromatograph equipped with a tritium electron capture detector (GC-ECD) and a 12 in x 0.125 in (o.d.) FEP Teflon column packed with 5% Carbowax 400 on Chromosorb G, 80/100 mesh. The nitrogen carrier flow was 75 ml min⁻¹ while the

column was kept at room temperature (approximately 293 K). A 100 ml sample was flushed through a 1.95 ml stainless steel loop and then transferred onto the column through a linear gas sampling valve. The chromatogram was complete in less than 4 minutes. Formaldehyde was analyzed by an improved chromatropic acid technique (Pitts et al. 1979).

For the 13-component surrogate- NO_x -air irradiations, analyses of the ΣC_6 hydrocarbons were also carried out by GC-FID using a 30 m SE-52 coated capillary column, temperature programmed from 223 to 473 K at 8 K min^{-1} .

NO_2 Actinometry. Light intensity in the 6400 liter indoor Teflon chamber irradiations was routinely monitored by measuring k_1 , the rate of photolysis of NO_2 , using the quartz flow tube technique of Zafonte et al. (1977). This involved measuring the amount of NO_2 converted to NO in N_2 when passed through the quartz tube at a known flow rate. The NO_2 photolysis rate is then given by

$$k_1 = \frac{\Delta[\text{NO}]}{[\text{NO}_2]} \cdot \frac{F}{V} \cdot \frac{1}{\phi}$$

where $\Delta[\text{NO}]$ is the measured increase in the NO concentration resulting from photolysis, $[\text{NO}_2]$ is the NO_2 concentration in the tube, F is the total flow rate through the tube (generally $\sim 3\text{ liter min}^{-1}$), V is the volume of the portion of the tube exposed to the photolyzing light, and ϕ is the effective quantum yield for the net production of nitric oxide upon photolysis. This effective quantum yield was calculated by Zafonte et al. (1977) to be 1.61 ± 0.07 under the range of reactant concentrations generally employed ($[\text{NO}_2] \approx 1\text{--}4\text{ ppm}$; $[\text{NO}]_0 \approx 0\text{--}0.3\text{ ppm}$). Zafonte et al. (1977) also calculated that no correction for refraction of light through quartz is necessary when a tubular reactor is employed.

The experiments carried out and the data obtained are described in the following section.

IV. RESULTS

As discussed in Section II above, the program was composed of the following elements: a) NO_x -air irradiations of the 13-component SAPRC-ARB modified surrogate organic mixture (Table II-1) which was designed to simulate the organic emissions in the South Coast Air Basin; b) development of a simplified 4- or 5-component mini-surrogate which yielded (within $\sim\pm 20\%$) the same ozone yields and overall reactivity as the 13-component surrogate; c) experimental investigation of organic reactivities by carrying out, using both single and dual-mode conditions, NO_x -mini-surrogate-air irradiations with incremental additions or deletions of the organics being studied (with the vast majority of the experiments being carried out under single-mode conditions); and d) chemical kinetic computer modeling of the single-mode experiments. The results from these research elements are discussed below.

A. NO_x -Air Irradiations of the SAPRC-ARB 13-Component Surrogate Mixture; Development of the 4-Component Mini-Surrogate Mixture, and Initial Experiments with Added Toluene

The irradiations carried out during this phase of the program and the initial NO_x and surrogate hydrocarbon concentrations are given in Table IV-1, together with selected observed reactivity parameters. The irradiations were carried out in the SAPRC indoor 6400 liter all-Teflon chamber, at 50% relative humidity, a temperature of 85°F (303 K) and with 100% of the maximum light intensity. The detailed data sheets are given in Appendix A.

The O_3 time-concentration profiles for the NO_x -air irradiations of the 13-component surrogate reached a plateau or peak within ~ 6 hrs of irradiation, and were hence suitable for comparison against the simplified mini-surrogate. The mini-surrogate was designed to have the same carbon content and OH radical reactivity as the 13-component SAPRC-ARB surrogate. It was also designed to have, to a good approximation, the same division with respect to both carbon content and OH radical reactivity, between the alkanes, alkenes, aromatics, and oxygenates as for the 13-component surrogate. Thus overall

Table IV-1. Irradiations Carried Out in the Indoor 6400 Liter All-Teflon Chamber to Develop a Four-Component Mini-Surrogate Mixture and Initial NO_x-Mini-Surrogate-Air Irradiations with Added Amounts of Toluene^a

ITC Run	Initial Concentrations				$\Delta([O_3]-[NO])/ \Delta t$ (ppb min ⁻¹)			Comments
	NO _x (ppm)	Surrogate (ppmC)	Toluene (ppm)	O ₃ max. at Time t (ppm)	(hr)	0-15 min	15-45 min	
393	0.383							NO _x -air
394								Propene-NO _x -air condition- ing run
395	0.479							NO _x -air
396	0.478							NO _x -air
397	0.185	1.80	-	0.225	6.0	2.40	2.13	13-component surrogate
398	0.198	3.30	-	0.364	6.0	2.27	2.33	13-component surrogate
399	0.107	3.33	-	0.261	5.5	3.40	3.67	13-component surrogate
400	0.113	1.74	-	0.234	5.75	1.60	2.07	13-component surrogate
401	0.186	3.49	-	0.356	6.0	2.53	3.70	13-component surrogate
402	0.446	-						NO _x -air
403	0.196	3.55	-	0.354	6.0	1.80	2.77	Mini-surrogate
404	0.117	3.68	-	0.234	5.0	2.00	2.77	Mini-surrogate
405	0.107	1.93	-	0.254	5.75	1.27	1.93	Mini-surrogate
406	0.123	3.48	-	0.261	6.0	1.40	3.10	Mini-surrogate
407	0.199	1.77	-	0.190	5.5	1.00	1.50	Mini-surrogate
408	0.126	3.69	0.150	0.212	2.75	2.20	2.87	Mini-surrogate + toluene
409	0.117	3.87	-	0.239	5.25	2.53	2.20	Mini-surrogate
410	0.559							NO _x -air
411	0.122	3.75	0.065	0.264	3.75	2.13	3.07	Mini-surrogate + toluene
412	0.106	3.63	0.185	0.212	~3.75	2.20	2.73	Mini-surrogate + toluene
413	0.106	3.60	-	0.246	~5.5	1.92	2.53	Mini-surrogate
414	0.113							NO _x -air

^a50% relative humidity, 100% lights (corresponding to an NO₂ photolysis rate constant k₁ of ~0.45 min⁻¹) and 303 K.

$$\left(\begin{array}{c} 4 \\ \sum_{i=1} n_i [\text{HC}_i] \\ \text{mini-surr.} \end{array} \right) = \left(\begin{array}{c} 13 \\ \sum_{i=1} n_i [\text{HC}_i] \\ \text{13-comp. surr.} \end{array} \right)$$

and

$$\left(\begin{array}{c} 4 \\ \sum_{i=1} k_i^{\text{OH}} [\text{HC}_i] \\ \text{mini-surr.} \end{array} \right) = \left(\begin{array}{c} 13 \\ \sum_{i=1} k_i^{\text{OH}} [\text{HC}_i] \\ \text{13-comp. surr.} \end{array} \right)$$

where n_i is the number of carbon atoms in hydrocarbon HC_i , $[\text{HC}_i]$ is the molar (i.e., by volume) concentration of hydrocarbon HC_i , and k_i^{OH} is its OH radical rate constant.

Based upon the organics present, their relative abundance in the 13-component surrogate (Table II-1), and their OH radical reactivities (Atkinson et al. 1979), n-butane was chosen as the representative alkane, propene as the representative alkene, m-xylene as the representative aromatic, and acetaldehyde as the aldehyde. The alkynes, represented by acetylene in the 13-component surrogate, were neglected because of the low OH radical reactivity (Atkinson et al. 1979) of acetylene.

Using this representation, i.e., a mini-surrogate consisting of n-butane, propene, m-xylene and acetaldehyde with the composition shown in Table IV-2, a mixture with a carbon content and OH radical reactivity essentially identical to that for the 13-component mixture was obtained.

NO_x -air irradiations of this 4-component mini-surrogate were then carried out in the 6400 liter all-Teflon chamber (Table IV-1) and the resulting O_3 , NO and NO_x time-concentration profiles were compared against those for the equivalent irradiations of the 13-component surrogate mixture. As shown by the data in Table IV-1, the NO_x -air irradiations of the mini-surrogate were in good agreement, within the scatter of the data, with the corresponding irradiations employing the 13-component surrogate. Hence it was concluded that this 4-component mini-surrogate was a totally adequate mixture for the investigation of organic reactivities.

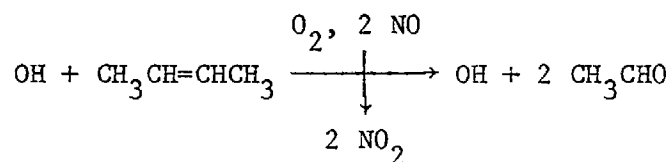
During this series of experiments, three NO_x -air irradiations of the mini-surrogate with varying amounts of added toluene were carried out to allow a preliminary assessment of this experimental approach. The initial conditions of these runs (ITC 408, 411 and 412) and selected reactivity data are given in Table IV-1 and summarized in Table IV-3. It can be seen

Table IV-2. Composition of the 4-Component Mini-Surrogate Chosen for Comparison Against the 13-Component SAPRC-ARB Surrogate

Organic	Mole %
n-Butane	70.8
Propene	16.9
m-Xylene	7.1
Acetaldehyde	5.2

that the effect of adding up to 1.3 ppmC toluene to ~4 ppmC of the mini-surrogate was relatively small, but that the addition of toluene did appear to decrease the maximum O_3 yields, while somewhat decreasing the time required to attain the maximum O_3 yields. The decreased time to attain the maximum O_3 could be due to toluene enhancing the rate of oxidation of NO to NO_2 (measured by $\Delta([O_3]-[NO])/At$, see Section IV.C). However, the initial NO oxidation rates observed in these experiments, summarized in Tables IV-1 and IV-3 for the time intervals 0-15 min and 15-45 min, were too scattered to indicate any effect of incremental toluene addition.

One reason for the relatively large scatter observed in the initial NO oxidation rates measured in these preliminary experiments could be the difficulties we encountered in reproducibly injecting acetaldehyde. Therefore, in order to improve the reproducibility of these experiments, it was decided to replace the acetaldehyde in the mini-surrogate with half the amount of trans-2-butene. trans-2-Butene reacts very rapidly with OH radicals to yield two molecules of acetaldehyde (Niki et al. 1978, Atkinson et al. 1979)



and its reaction with O_3 (the other major sink for trans-2-butene under these conditions) also gives rise to acetaldehyde as its major carbon-containing product. Chemical kinetic computer model calculations

Table IV-3. Effect of Adding Various Concentrations of Toluene to an Irradiated NO_x (~0.1 ppm)-4-Component Surrogate (~4 ppmC)-Air Mixture

ITC Run	Added Toluene Concentration (ppm)	O ₃ Max (ppm)	Time to O ₃ Max (mins) ^a	$\Delta([O_3]-[NO])/ \Delta t$ (ppb min ⁻¹)	
				0-15 min	15-45 min
404-413 ^b	0	0.23-0.25 ^b	240-360 ^b	1.4-2.5	2.5-3.1
411	0.065	0.264	210-240	2.1	3.1
	0.150	0.212	150-180	2.2	2.9
	0.185	0.212	180-270	2.2	2.7

^aO₃ decreased only slowly after attaining a maximum, hence time to maximum was ill-defined.

^bRange observed in four replicate irradiations (ITC 404, 406, 409 and 413).

(described in Section IV.D) showed that this substitution caused a slight enhancement in the NO oxidation rate, but did not noticeably effect the maximum ozone yield (see Figure IV-1). Since this effect was relatively small, and since reproducibility of injections is critically important in order to assess relatively small changes of reactivity in a series of single-mode experiments, all subsequent experiments were done using 2.6 mole % trans-2-butene instead of the 5.2 mole % acetaldehyde listed in Table IV-2.

B. Dual-Mode NO_x-Air Irradiations

After the development of this modified mini-surrogate, a series of NO_x-air irradiations, with and without added toluene, were then carried out in the SAPRC outdoor ~40,000 liter chamber. The chamber was used in the dual-mode configuration, as described in Section III above, and the irradiations carried out are listed in Table IV-4. Two of these irradiations (OTC-136 and 140) were carried out with the mini-surrogate in both sides, in order to test the equivalency of the two sides of the chamber. For the runs with added toluene, the side to which the toluene was added was also varied in order to minimize any memory effects. The initial conditions for these dual-mode irradiations are summarized in Table IV-4 and the ozone time-concentration profiles obtained during these irradiations are shown in Figures IV-2 and IV-3.

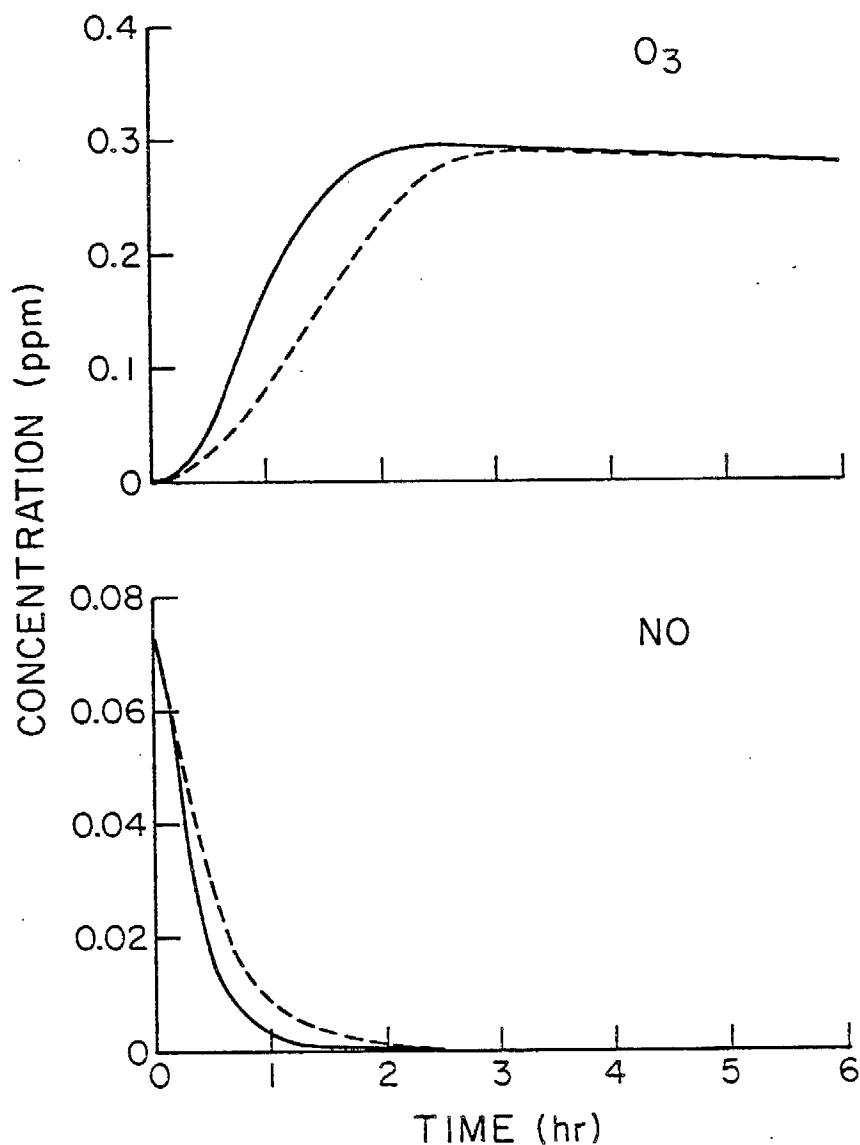


Figure IV-1. Calculated O_3 and NO Time-Concentration Profiles for the Irradiated Mini-Surrogate- NO_x -Air Systems Showing the Effect of Replacing Acetaldehyde by Half the Amount of trans-2-Butene: --- Mini-Surrogate with Acetaldehyde Included; — Mini-Surrogate with Acetaldehyde Replaced by Half the Amount of trans-2-Butene.

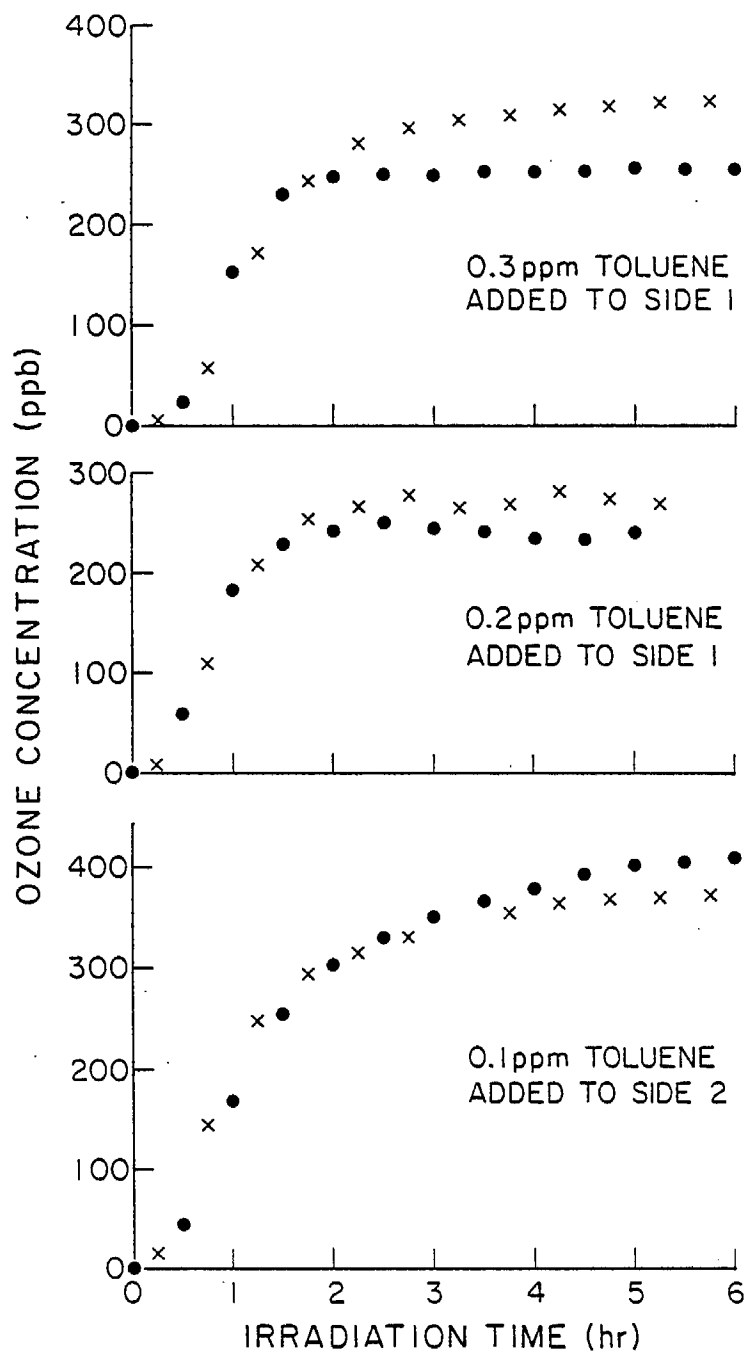


Figure IV-2. O₃ Time-Concentration Profiles for NO_x-Organic-Air Dual-Mode Photooxidations; Surrogate Versus Surrogate.
 ● - Side 1, x - Side 2.

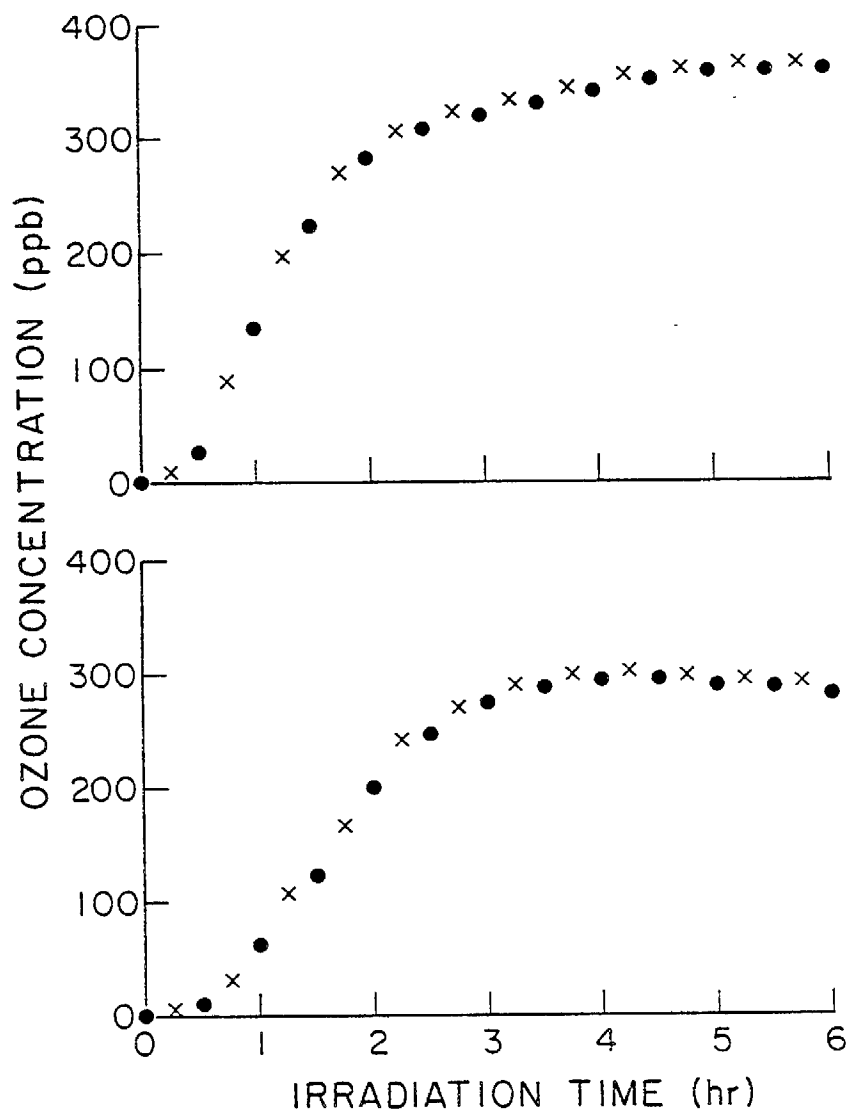


Figure IV-3. O_3 Time-Concentration Profiles for NO_x -Organic-Air Dual-Mode Photooxidations; Surrogate Versus Surrogate + Added Toluene. • - Side 1, x - Side 2.

Table IV-4. Initial Conditions of Dual-Mode Outdoor NO_x-Hydrocarbon-Air Irradiations

OTC Run No.	Side 1	Side 2
136	4 ppmC surrogate	4 ppmC surrogate
137	4 ppmC surrogate + 0.22 ppm toluene	4 ppmC surrogate
139	4 ppmC surrogate	4 ppmC surrogate + 0.10 ppm toluene
140	4 ppmC surrogate	4 ppmC surrogate
141	4 ppmC surrogate + 0.30 ppm toluene	4 ppmC surrogate

From Figure IV-2 it can be seen that, in agreement with the initial single-mode indoor chamber experiments discussed previously and with the subsequent experiments discussed in the following section, the addition of toluene decreases the maximum O₃ yields, but increases the initial rate of O₃ formation and (not shown here) of NO oxidation. Figure IV-3 shows that the two surrogate versus surrogate runs show good side-to-side equivalency, confirming that the differences observed in Figure IV-2 cannot be due to experimental artifacts. Hence we can conclude that while toluene has "positive" reactivity in terms of enhancing rates of O₃ formation and NO oxidation, it has a "negative" reactivity in the sense that its addition tends to reduce the maximum O₃ yields. These observations are discussed in more detail in Section V.

Outdoor dual-mode chamber experiments such as these are probably more sensitive than consecutive single-mode experiments in determining quantitative effects of incremental addition, since the "control" irradiation is carried out at the same time and with the same temperature, light intensity, humidity and initial reactant concentrations (other than that of the organic being tested). However, such experiments are not particularly well suited for routine assessment of reactivities of organics. In particular, outdoor chamber irradiations are inherently less reproducible than indoor chamber runs, making comparison of incremental reactivity for different compounds measured in different experiments more uncertain, and the indoor chamber facility of the California Air Resources Board at El

Monte is not suitable for conducting dual-mode irradiations. For this reason, the great majority of the experiments conducted under this program consisted of single-mode irradiations in the indoor SAPRC 6400 liter Teflon chamber, as discussed in the following section. However, the outdoor, dual-mode irradiations described above were useful in showing that the same qualitative incremental reactivity effects can be obtained both in dual-mode experiments and in consecutive single-mode experiments such as those discussed below.

C. Incremental Reactivity Determinations Employing Single-Mode NO_x-Air Irradiations of the Mini-Surrogate

The majority of the experiments conducted under this program for the purpose of assessing reactivity effects consisted of alternating replicate standard mini-surrogate-NO_x-irradiations with mini-surrogate-NO_x irradiations with varying amounts of test organics added or (in the case when the test organic was also a mini-surrogate component) removed. Interdispersed among these mini-surrogate-NO_x irradiations were tracer-NO_x-air control irradiations and NO₂ actinometry experiments. The test organics studied in this series of experiments were toluene, benzaldehyde, ethanol, methanol, tert-butyl methyl ether (TBME), and the mini-surrogate components n-butane, propene, and trans-2-butene.

These irradiations were carried out in the 6400 liter indoor Teflon chamber (ITC) at 50% relative humidity and 85°F (303 K) and with a light intensity of 70% of the maximum. This light intensity was chosen since initial experiments in this particular series of experiments showed that use of 100% lights led to somewhat elevated temperatures (>90°F) and O₃ time-concentration profiles which did not exhibit a maximum, but rather increased slowly and monotonically with the irradiation time. While not totally understood, this effect may have been due to enhanced NO_x permeation from room air at these higher temperatures. However, after installation of further cooling capacity and by operating at 70% of the maximum light intensity, irradiations of NO_x-hydrocarbon-air mixtures yielded O₃ time-concentration profiles which increased with irradiation time to a constant plateau value, much like the data obtained in the development of the mini-surrogate (Section IV.A above).

The "standard" mini-surrogate-NO_x mixture consisted of nominal initial concentration of 4 ppmC hydrocarbon and 0.1 ppm NO_x with the initial NO/NO₂ ratio being 4. Except for the levels of the test organic, the initial concentrations of the other components of the mini-surrogate mixture were the same as those in the standard runs. The averages of the measured initial concentrations for all experiments in this series (except for cases when an initial surrogate component level was deliberately varied to assess its incremental reactivity) are summarized in Table IV-5 for the groups of consecutive experiments ITC 450-503 and ITC 578-613, as well as for all experiments in this series, with the standard deviations giving a measure of the reproducibility of the injections. It can be seen that reasonably good reproducibility in initial concentrations was attained.

A chronological listing of the mini-surrogate and control experiments is given in Table IV-6, and detailed data tabulations are given in Appendix A. Also included in Table IV-6 are selected results of the tracer-NO_x-air and the NO₂ actinometry control experiments, as well as (for the standard and modified surrogate-NO_x runs) several measurements of overall reactivity, such as the maximum O₃ yields, NO oxidation rates, and estimated average hydroxyl radical levels.

Table IV-5. Averages^a of Measured Initial Reactant Concentrations in Replicate Mini-Surrogate-NO_x Irradiations ITC 450-503 and ITC 578-613

Compound	Average Initial Concentration (ppb)		
	ITC 450-503	ITC 578-613	Overall
NO	72 ± 4	79 ± 5	75 ± 6
NO ₂	22 ± 5	19 ± 3	21 ± 4
NO _x	94 ± 3	98 ± 5	95 ± 5
Propene	166 ± 5	162 ± 18	165 ± 11
n-Butane	701 ± 20	696 ± 35	699 ± 24
m-xylene	72 ± 3	68 ± 2	70 ± 3
trans-2-butene	25.3 ± 1.2	25.4 ± 1.6	25.3 ± 1.3

^aIncluded measurements made in experiments with added or reduced test organic, excluding the measured levels of the varied organic. Errors shown are single standard deviations of the average.

Table IV-6. Chronological Listing and Selected Results of Mini-Surrogate-NO_x^a and Associated NO_x-Air^b and Actinometry Experiments Carried Out in the Indoor Teflon Chamber to Study Incremental Reactivity Effects

ITC Run No.	Species Added Name (ppb)	Surrogate Runs ^c			NO _x -Air Run		NO ₂ Actinometry		
		Maximum ^d O ₃ (ppb)	Average ^e [OH] (10 ⁶ cm ⁻³)	$\frac{\Delta([O_3]-[NO])/\Delta t}{t=0-15 \text{ min} \quad t=15-45 \text{ min}}$ (ppb min ⁻¹)	ITC Run No.	Radical ^f Source (ppb min ⁻¹)	-d[NO]/dt ^f (ppb min ⁻¹)	ITC Run No.	k ₁ ^g (min ⁻¹)
450	-		2.34	1.80	448	0.053	0.11	441	0.423
451	Toluene	180	(2.31)	(2.00)					
452	-		2.31	1.80	453	0.044	0.09	454	0.376
455	Toluene	89	(2.30)	(1.46)					
456	-		2.35	1.47					
457	Benzaldehyde	1	(1.18)	(0.27)	460	0.056	0.09	458	0.378
459	-		2.30	1.87					
461	-		-	1.53					
462	Benzaldehyde	518	(0.43)	(0.07)	463	0.056	0.09	464	0.369
465	-		2.44	1.93					
466	Benzaldehyde	347	(0.65)	(0.40)					
467	-		2.36	1.40					
468	Benzaldehyde	115	(1.17)	(0.60)	469	0.055	0.11	470	0.380
471	-		2.25	1.67					
472	Propene	-166	(2.93)	(1.27)					
473	-		2.30	1.40					
474	Propene	113	(1.99)	(1.67)	475	0.051	0.14	476	0.342
477	-		2.30	-					
478	Propene	334	(1.77)	(2.40)	480	0.058	0.14	481	0.334
479	-		2.49	1.53					
482	n-Butane	-701	(3.26)	(1.27)					
483	-		2.41	2.00	485	0.081	0.11	486	0.352
487	-		2.26	1.27					
488	n-Butane	483	(1.96)	(1.60)					
489	-		2.31	1.73	490	0.057	0.10	491	0.331
492	n-Butane	1009	(1.77)	(1.60)					
493	-		2.29	2.09					
494	n-Butane	1129	(1.77)	(1.47)	496	0.045	0.09	495	0.348
497	-		2.40	1.20					
498	trans-2-Butene	-25.3	(2.39)	(1.33)					
499	-		2.31	1.60					
500	trans-2-Butene	58.9	(2.01)	(3.55)					
501	-		2.28	1.60					
502	trans-2-Butene	163	(1.71)	(7.18)					

Table IV-6 (continued) - 2

ITC Run No.	Species Added Name	Surrogate Runs ^c				NO _x -Air Run		NO ₂ Actinometry		
		Maximum ^d O ₃ (ppb)	Average ^e [OH] (10 ⁶ cm ⁻³)	Δ([O ₃]-[NO])/Δt (ppb min ⁻¹)		ITC Run No.	Radical ^f Source (ppb min ⁻¹)	-d[NO]/dt ^f (ppb min ⁻¹)	ITC Run No.	k ₁ ^g (min ⁻¹)
				t=0-15 min	t=15-45 min					
503	-	325	2.37	1.40	3.67	504	0.041	0.12	505	0.324
578	-	351	2.10	1.53	2.77	577	0.049	0.09	576	0.301
579	Propene	(355)	(2.80)	(0.73)	(1.80)					
580	-	354	2.32	1.53	2.43					
581	Propene	(351)	(1.95)	(2.13)	(4.43)	582	0.038	0.11	583	0.315
584	-	374	2.29	1.87	3.30					
585	Propene	(311)	-	(3.00)	(6.70)					
586	-	352	1.93	1.40	4.03					
587	Ethanol	(373)	(1.73)	(2.13)	(4.73)	588	0.070	0.15	589	0.320
590	-	370	2.18	0.93	3.37					
591	Ethanol	(402) ^h	(1.47)	(2.07)	(4.10)					
592	-	361 ^h	2.13	(0.80)	(3.43)					
593	Ethanol	(354)	(1.19)	(2.40)	(4.87)	595	0.071	0.28	594	0.271 ^l
597	-	342	2.11	1.13	3.63	600	0.071	0.12	596	0.276 ^l
598	-	366	2.13	1.27	3.77				601	0.275 ^l
602	TBME ^k	(372)	(1.67)	(1.93)	(4.37)	605	0.062	0.12	604	0.300
603	-	332	2.15	1.27	3.63					
606	TBME	(432) ^h	(1.53)	(1.27)	(4.73)					
607	-	382	2.17	0.73	3.07					
608	TBME	(417)	(1.23)	(2.60)	(3.43)	610	0.072	0.10	611	0.312
609	-	365	2.18	0.93	3.20					
612	Methanol	(361)	(2.12)	(1.00)	(3.40)	614	0.055	0.10	615	0.313
613	-	336	2.03	1.33	3.20					

^aInitial NO_x \approx 0.1 ppmC, surrogate (standard runs) = 4 ppmC; 70% lights, 50% relative humidity, 303 K. Six-hour runs.

^bSame conditions as standard mini-surrogate-NO_x runs except surrogate replaced by ~10 ppb each of propene and n-butane. Two-hour runs.

^cResults for runs with species added or removed indicated in parentheses to distinguish from results of repeated standard surrogate runs.

^dExcept as noted, maximum O₃ observed when run was terminated after 6 hours irradiations.

^eCalculated from initial and final m-xylene concentrations using equation IV.

^fCalculated for t=60-120 minutes as described by Carter et al. (1982a).

^gCalculated using formula of Holmes et al. (1973), using updated rate constants (Atkinson and Lloyd 1983).

^hTrue maximum occurred prior to end of run.

ⁱDiscrepancy between amount injected and GC data. Concentration unknown.

^jRun ITC 487 gave anomalously low O₃. Results not used in subsequent data analysis.

^ktert-Butyl methyl ether.

^lSeveral lamps subsequently found to be off; this may account for low k₁ value.

^mEstimated based on amount injected.

The results of the actinometry experiments, though somewhat scattered, indicate a continual decline of the NO_2 photolysis rate, k_1 , from $\sim 0.35 \text{ min}^{-1}$ from the beginning of this series to $\sim 0.31 \text{ min}^{-1}$ around the end of these runs. These k_1 measurements are plotted against the run number in Figure IV-4 for the time period involving these experiments, and the curve shown in that figure gives the "best estimate" k_1 values as a function of run number (for the runs with 70% lights). The anomalously low values around ITC 600 are probably due to several malfunctioning lamps discovered during that period, and it affects only a few experimental runs in this series (ITC 597 through 603); the reason for the anomalously high measurement of ITC 551 is not known, but this was during the time between the two sets of experiments of interest here.

Table IV-6 also summarizes the radical input rates and the NO oxidation rates observed in the tracer- NO_x -air control irradiations. The "radical input rate" is defined as the input rate of hydroxyl radicals from chamber-dependent sources required to account for the observed consumption rate of the hydrocarbon tracers (assuming the only significant radical sink in NO_x -air systems is reaction of hydroxyl levels with NO_2). The radical input rate is discussed in detail by Carter et al. (1982a) and Pitts et al. (1983), and thus need not be detailed here except to note that this quantity must be known in order to computer model these experiments (see Section IV.D). The results of these experiments indicate that there was no significant variation in the radical input rates during this experimental program [the variability in the radical input rates given in Table IV-6 is well within the normal variability typical of these measurements (Carter et al. 1982a, Pitts et al. 1983)]. The overall average radical input rate of $0.056 \pm 0.013 \text{ ppb min}^{-1}$ can thus be assumed to apply to all runs within this series for computer modeling purposes.

The NO oxidation rates observed in these tracer- NO_x -air irradiations are also useful to assess chamber contamination by reactive organics, since the presence of such contaminants significantly enhances these rates (Carter et al. 1982a, Pitts et al. 1983). The NO oxidation rates observed in the tracer- NO_x -air runs summarized in Table IV-6 are relatively low and showed no significant tendency to increase throughout the series. This indicates that contamination effects were not a problem in these experiments.

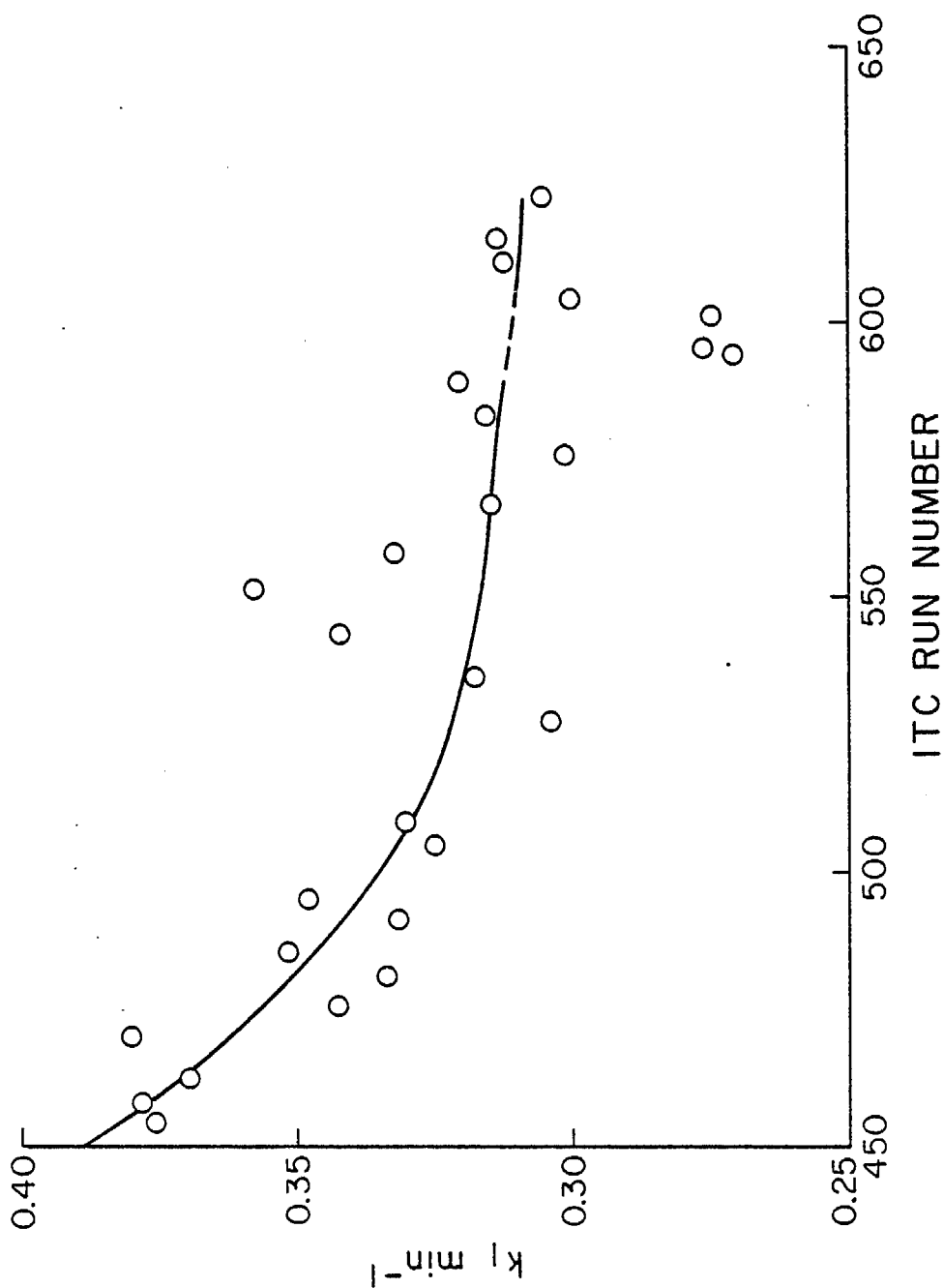


Figure IV-4. Plot of the NO₂ Photolysis Rate, k_1 , in the Indoor Teflon Chamber (70% Light) Against the Run Number.

Three types of measurements of overall reactivity in the standard and modified mini-surrogate runs are summarized in Table IV-6, and these are used as the basis for defining incremental reactivities of the test organics. These are discussed briefly below:

(1) Maximum O_3 yield. This is simply the highest O_3 level observed during the six hours of irradiation. As discussed previously, in most experiments the O_3 increased rapidly after the NO was consumed and then leveled off and increased only slowly with time for the remainder of the experiment. The highest reading generally occurred when the run was terminated at $t = 6$ hours, so the reported values are not "true" maxima; but, since the increase was slow, these can be considered to be reasonable approximations of the "true" maxima. For a few experiments, the O_3 gradually declined following the period of rapid increase, and in those cases the reported values are indeed "true" maxima. (Footnotes in Table IV-4 indicate when this was the case.) In no case was the O_3 rapidly increasing when the run was terminated, so the tabulated O_3 "maxima" reflect only the maximum O_3 forming potential, and not the rate at which it was formed.

(2) NO oxidation rates. The formation of O_3 in organic- NO_x -air irradiations is caused by the conversion of NO to NO_2 by the intermediate peroxy radicals formed when the organic is photooxidized, and the rate at which this conversion occurs is another manifestation of reactivity. This is most conveniently measured by the rate of change in the quantity ($[O_3] - [NO]$), since this reflects both the rate of NO consumption and the rate of O_3 formation. In our surrogate- NO_x irradiations, the quantity ($[O_3] - [NO]$) was observed to increase relatively slowly for the first 15 minutes, then at a more rapid, fairly constant rate for the following 30-60 minutes, and then more slowly again as the maximum ozone level is approached. Therefore, the quantities $\Delta([O_3] - [NO])/\Delta t$ are reported separately in Table IV-6 for the periods 0-15 minutes and 15-45 minutes, these being sufficiently early periods in the run that the rate is not directly affected by the maximum O_3 yield.

(3) Average hydroxyl radical levels. The photooxidation of the test organics can also possibly enhance or suppress radical levels in NO_x -air irradiations, and this can thus be considered to be another aspect of reactivity of the organics. Hydroxyl radical levels can be measured in

these experiments by the amount of m-xylene consumed during the irradiations, since reaction with OH radicals is believed to be its only significant loss process in these systems (Atkinson et al. 1979, Atkinson and Lloyd 1983). Additionally, though not critical, the initial concentrations of m-xylene were essentially the same in all the mini-surrogate-NO_x irradiations discussed in this section. Since dilution in these indoor Teflon chamber irradiations is assumed to be small (due to the flexible nature of the bag reactor which collapses as sample is withdrawn), we can write:

$$\frac{-d[\text{m-xylene}]}{dt} = k_{\text{OH} + \text{m-xyl}} [\text{OH}] [\text{m-xylene}] \quad (\text{I})$$

which can be integrated and re-arranged to obtain

$$\int_{t_0}^t [\text{OH}] dt = \frac{1}{k_{\text{OH} + \text{m-xyl}}} \ln \left(\frac{[\text{m-xylene}]_{t_0}}{[\text{m-xylene}]_t} \right) \quad (\text{II})$$

where $k_{\text{OH} + \text{m-xyl}}$ is the OH + m-xylene rate constant, known to be $2.38 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ (Atkinson et al. 1979), $[\text{m-xylene}]_{t_0}$ is the initial m-xylene concentration, and $[\text{m-xylene}]_t$ is the final m-xylene concentration in these 360 minute irradiations. The average OH concentration for the run, $\langle \text{OH} \rangle$, is given by

$$\langle \text{OH} \rangle = \frac{1}{(t-t_0)} \int_{t_0}^t [\text{OH}] dt \quad (\text{III})$$

and

$$\langle \text{OH} \rangle = \frac{1}{(t-t_0) \cdot k_{\text{OH} + \text{m-xyl}}} \cdot \ln \left(\frac{[\text{m-xylene}]_{t_0}}{[\text{m-xylene}]_t} \right) \quad (\text{IV})$$

The values of $\langle \text{OH} \rangle$ estimated in this way are also summarized in Table IV-6.

As discussed in Section II, the quantities of interest which these experiments are designed to measure are the incremental reactivities, $I_R^{\Delta[\text{organic}]}$, which are given by

$$I_R^{\Delta[\text{organic}]} = \frac{R^{\Delta[\text{organic}]} - R^0}{\Delta[\text{organic}]} \quad (\text{VI})$$

where R refers to an overall reactivity measurement of interest (in this case, maximum O_3 yields, NO oxidation rates, $\Delta([\text{O}_3]-[\text{NO}])/\Delta t$, over the time periods 0-15 minutes or 15-45 minutes, and the average hydroxyl radical concentrations), R^0 is the equivalent measurement in the standard mini-surrogate runs, and $R^{\Delta[\text{organic}]}$ is the corresponding reactivity measurement when the concentration of the test compound is changed by an amount $\Delta[\text{organic}]$ from that present in the standard mixture. The precision with which $I_R^{\Delta[\text{organic}]}$ can be measured for a given type of reactivity measurement obviously depends on how well defined R^0 is, since any reactivity measurement will vary with repeated standard surrogate- NO_x irradiations, as can be seen from Table IV-6.

The variabilities of the reactivity measurements in the standard mini-surrogate runs are illustrated in Figures IV-5 through IV-7, where maximum O_3 yields, 0-15 and 15-45 min values of $\Delta([\text{O}_3]-[\text{NO}])/\Delta t$, and $\langle \text{OH} \rangle$ values are plotted against run number. It can be seen that, except possibly for the dip in the maximum O_3 yields and the 15-45 min NO oxidation rates around the period of runs ITC 467-473 (which may be due to an effect of benzaldehyde contamination) the scatter in these measurements are essentially random in nature.

In order to obtain an estimate of the best value of R^0 to associate with a particular run in which the test organic was varied, linear regression analyses of the reactivity parameters against run number were carried out for groups of runs in which the scatter was judged (subjectively) to be due only to random fluctuations (as opposed to the apparent benzaldehyde contamination effect), and the resulting lines are also shown in Figures IV-5 through IV-7. These lines were then used to determine the values of R^0 associated with any given run in which a test organic was added or varied. The uncertainties associated with those values are the standard deviations of the dependent variable derived from the regression or (in a few cases when the standard deviation from the regression appeared to be unrealistically low to reflect the probable scatter) subjective estimates made based on the scatter observed in Figures IV-5 through IV-7.

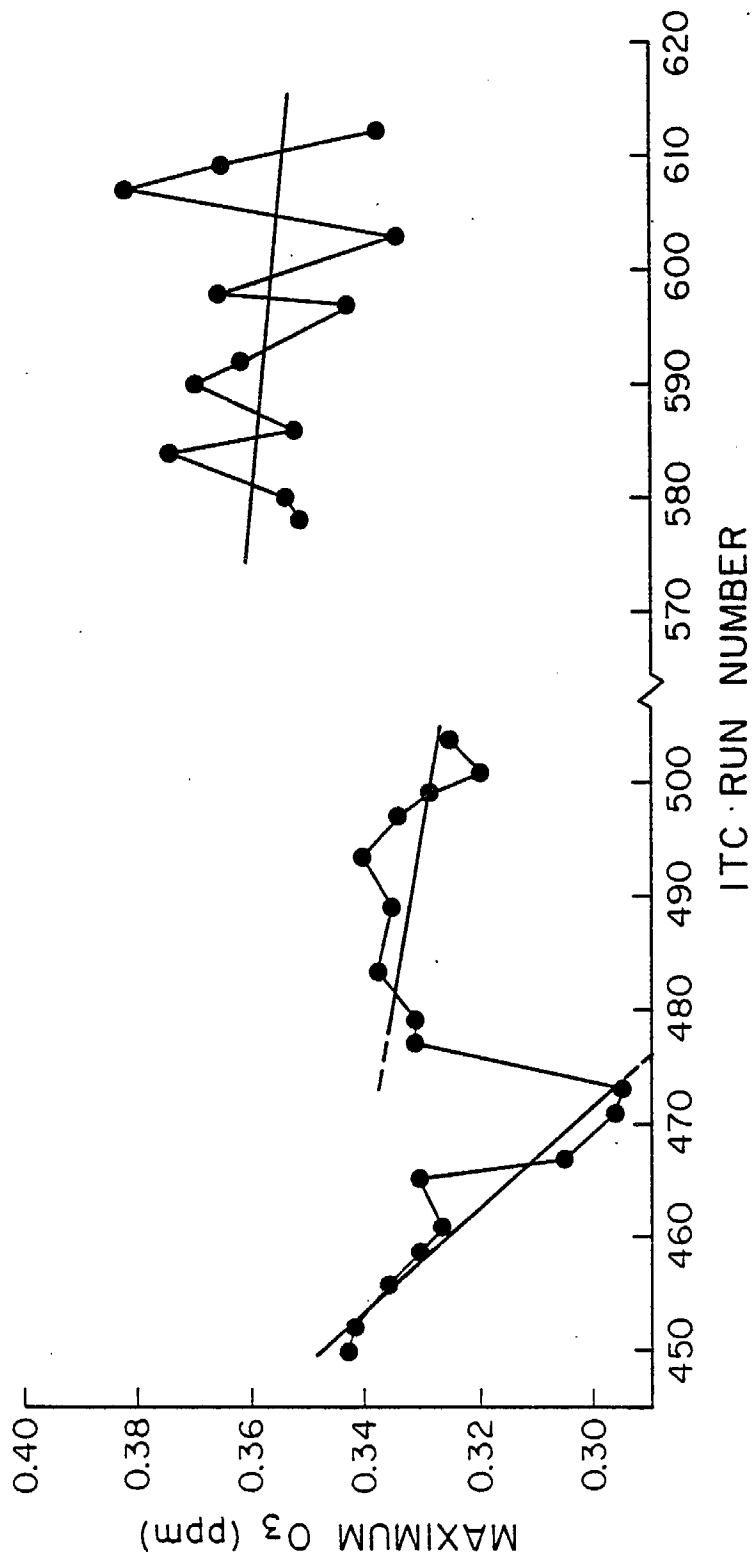


Figure IV-5. Plot of the Maximum O₃ Yield Observed in the Standard Mini-Surrogate-NO_x Runs Carried Out in the Indoor Teflon Chamber Against Run Number.

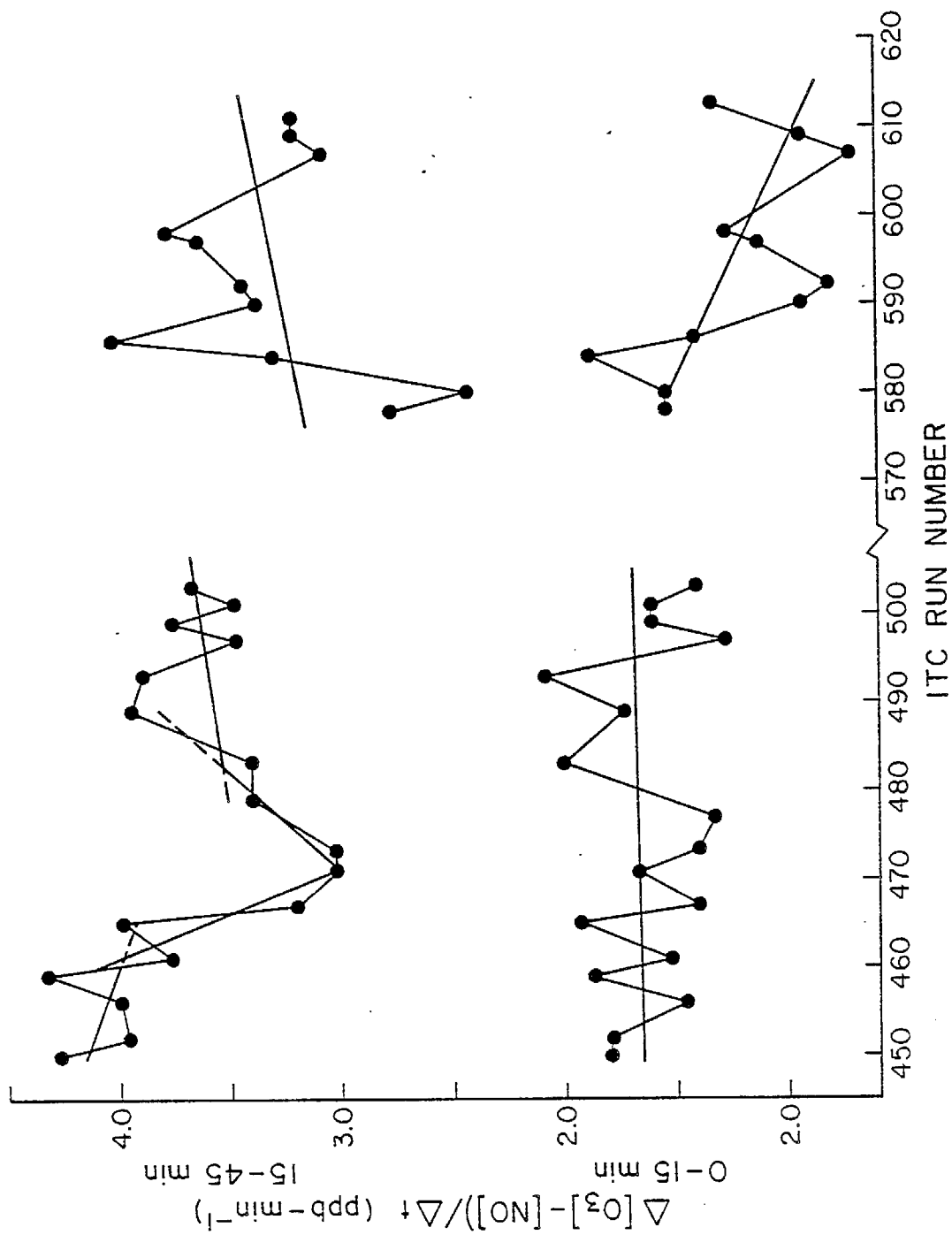


Figure IV-6. Plots of the 0-15 Minute and the 15-45 Minute $\Delta[O_3] - [NO] / \Delta t$ Values Observed in the Standard Mini-Surrogate- NO_x Runs Carried Out in the Indoor Teflon Chamber Against Run Number.

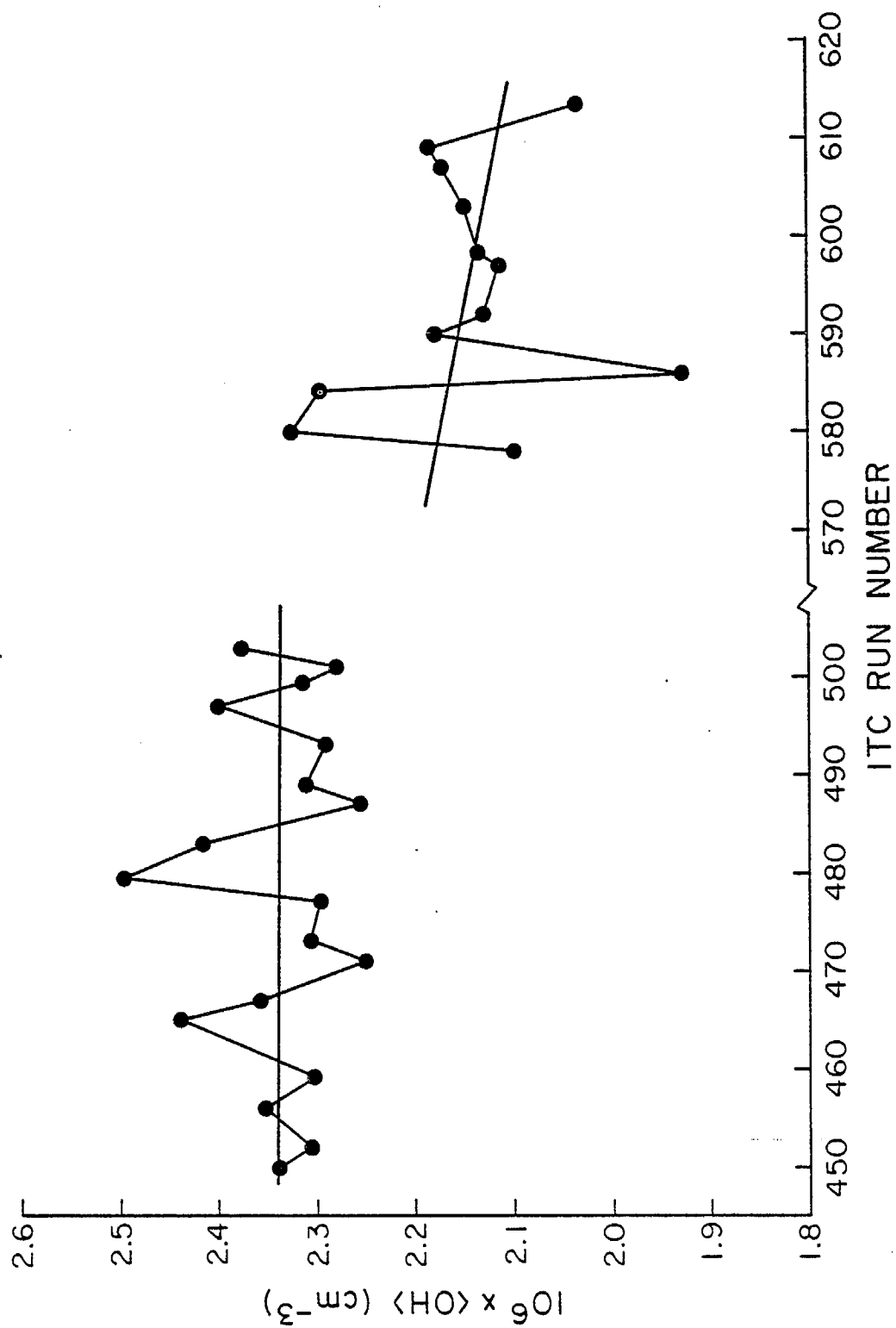


Figure IV-7. Plots of the Average Hydroxyl Radical Concentration, Calculated Using Equation (I), Observed in the Standard Mini-Surrogate- NO_x Runs Carried Out in the Indoor Teflon Chamber Against Run Number.

Table IV-7 summarizes the reactivity measurements, $R^{\Delta[\text{organic}]}$, observed in the experiments in which the test organics were added or varied, the values of R^0 associated with those experiments taken from the regression lines shown in Figures IV-5 through IV-7 and their associated (single standard deviation) uncertainties, and the quantities $I_R^{\Delta[\text{organic}]}$ derived from those values using equation II. The single-standard deviation uncertainties given for the $I_R^{\Delta[\text{organic}]}$ values in Table IV-7 are derived based on the assumption that the uncertainty of R^{obs} is the same as that derived for R^{std} , and that the uncertainties in these values are much greater than those associated with $\Delta[\text{organic}]$. It can be seen that in many cases the magnitude of the uncertainty estimates were greater than the magnitude of the $I_R^{\Delta[\text{organic}]}$ values, but in some runs, generally those with larger values of $\Delta[\text{organic}]$, the $I_R^{\Delta[\text{organic}]}$ values are relatively well determined.

As discussed in Section II, the quantity of interest that these experiments are designed to measure are the limiting incremental reactivities, I_R^0 , given by:

$$I_R^0 = \lim_{\Delta[\text{organic}] \rightarrow 0} (I_R^{\Delta[\text{organic}]}) \quad (\text{VII})$$

Thus in order to derive these values, it is necessary to extrapolate the values of $I_R^{\Delta[\text{organic}]}$ to $\Delta[\text{organic}] = 0$. Plots of the $I_R^{\Delta[\text{organic}]}$ values from Table IV-7 against $\Delta[\text{organic}]$ are shown in Figures IV-8 through IV-15 for each of the eight test organics studied in this series of experiments. It can be seen that in many cases the high estimated uncertainties in the $I_R^{\Delta[\text{organic}]}$ values, particularly for the experiments with low levels of $\Delta[\text{organic}]$ and for those with the less reactive organics whose $I_R^{\Delta[\text{organic}]}$ values have relatively low magnitudes even in runs with high $\Delta[\text{organic}]$ values, make this extrapolation extremely uncertain. In those cases the dependence of $I_R^{\Delta[\text{organic}]}$ on $\Delta[\text{organic}]$ cannot be determined on the basis of these data, and I_R^0 can only be estimated as the weighted average of the $I_R^{\Delta[\text{organic}]}$ values. In other cases, estimates by weighted least squares linear regression can be made, and, although in general the dependence of $I_R^{\Delta[\text{organic}]}$ on $\Delta[\text{organic}]$ would not be expected to be linear, the quantity and quality of these data make assumptions of more complex functional dependencies unjustified. The

Table IV-7. Changes in Reactivity Due to Incremental Additions or Removal of Various Test Organics in Mini-Surrogate-NO_x-Air Irradiations in the 5800 Å Indoor Teflon Chamber^a

Organic		Maximum O ₃		0-15 min Δ([O ₃]-[NO])/Δt		15-45 min Δ([O ₃]-[NO])/Δt		Estimated [OH] avg ^d	
ITC Run No.	Added or Removed (ppb)	Obs. (ppb)	Std. ^b (ppb)	Obs-Std ^c Δ[organic]	Obs. (ppb min ⁻¹)	Std. ^b (ppb min ⁻¹)	Obs-Std ^c Δ[organic] (10 ⁻³ min ⁻¹)	Obs. (10 ⁶ cm ⁻³)	Std. ^b (10 ⁶ cm ⁻³)
								Obs-Std ^c Δ[organic] (10 ⁶ cm ⁻³) ppm ⁻¹	
						</			

Table IV-7 (continued) - 2

Organic [TC Added or Run Removed No. (ppb)]	Maximum O ₃			0-15 min $\Delta([O_3]-[NO])/At$			15-45 min $\Delta([O_3]-[NO])/At$			Estimated [OH] avg ^d		
	Obs. (ppb)	Std. b (ppb)	Obs-Std ^c $\Delta[organic]$	Obs. (ppb min ⁻¹)	Std. b (ppb min ⁻¹)	Obs-Std ^c $\Delta[organic]$ (10 ⁻³ min ⁻¹)	Obs. (ppb min ⁻¹)	Std. b (ppb min ⁻¹)	Obs-Std ^c $\Delta[organic]$ (10 ⁻³ min ⁻¹)	Obs. (10 ⁶ cm ⁻³)	Std. b (10 ⁶ cm ⁻³)	Obs-Std ^c $\Delta[organic]$ (10 ⁶ cm ⁻³)
<u>trans-2-Butene</u>												
498 -25.3	311	329 ± 6	0.7 ± 0.3	1.3	1.7 ± 0.2	33 ± 6 ^f	3.5	3.7 ± 0.2	44 ± 12	2.39	2.34 ± 0.07	-4.0 ± 0.8 ^g
500 59	326	329 ± 6	-0.04 ± 0.14	3.6	1.7 ± 0.2	32 ± 6	6.3	3.7 ± 0.2	45 ± 5	2.01	2.34 ± 0.07	-2 ± 4
502 163	309	328 ± 6	-0.12 ± 0.05	7.2	1.7 ± 0.2	34 ± 2	5.5	3.7 ± 0.2	11 ± 2	1.71	2.34 ± 0.07	-5.6 ± 1.6
<u>Ethanol</u>												
587 888	373	358 ± 16	0.02 ± 0.03	2.1	1.3 ± 0.3	0.8 ± 0.3 ^g	4.7	3.2 ± 0.5	1.7 ± 0.7	1.73	2.16 ± 0.11	-0.52 ± 0.09 ^g
591 986	402	358 ± 16	0.05 ± 0.02	2.1	1.3 ± 0.3	0.9 ± 0.5	4.1	3.3 ± 0.5	0.8 ± 0.7	1.47	2.15 ± 0.11	-0.48 ± 0.17
593 1963	354	357 ± 16	-0.002 ± 0.012	2.4	1.2 ± 0.3	0.6 ± 0.2	4.9	3.3 ± 0.5	0.8 ± 0.3	1.19	2.15 ± 0.11	-0.69 ± 0.15
<u>t-Butyl methyl ether</u>												
602 965	372	356 ± 16	0.008 ± 0.012	1.9	1.1 ± 0.3	0.5 ± 0.3 ^g	4.4	3.4 ± 0.5	0.5 ± 0.3	1.67	2.13 ± 0.11	0.34 ± 0.05 ^g
606 1840	432	355 ± 16	0.042 ± 0.012	1.3	1.0 ± 0.3	0.4 ± 0.2	4.7	3.4 ± 0.5	0.7 ± 0.4	1.53	2.12 ± 0.11	-0.47 ± 0.16
608 2685	417	355 ± 16	0.023 ± 0.008	2.6	1.0 ± 0.3	0.60 ± 0.16	3.4	3.4 ± 0.5	0.0 ± 0.2	1.23	2.12 ± 0.11	-0.32 ± 0.08
<u>Methanol</u>												
612 ~1000	361	354 ± 16	0.01 ± 0.02	1.0	0.9 ± 0.3	0.1 ± 0.4	3.4	3.4 ± 0.5	0.0 ± 0.7	2.12	2.12 ± 0.11	-0.33 ± 0.06
												+0.01 ± 0.15

a₁=303 ± 2 K, k₁ = 0.31-0.38 min⁻¹ (see Figure IV-4), ~4 ppmC mini-surrogate (standard), 0.1 ppm NO_x (see Table IV-6), 50% RH.

^bDerived from least squares regression lines against Run number shown in Figures IV-5 through IV-7 for appropriate reactivity parameter. Error given is single standard deviation of estimated reactivity measurement regression line.

^cError given is single standard deviation assuming that uncertainty in value measured in run with varied organic is the same as uncertainty given for value of reactivity in "standard" run, neglecting any uncertainty in [Organic]. Estimated limiting value as [Organic]→0 is given in brackets above the experimental values.

^dEstimated from amount of m-xylene consumed as described in text.

^eSimple average of the two experimental values. Error given is single standard deviation of the average.

^fIntercept from weighted linear least squares regression. Error given is estimated single standard deviation of the intercept.

^gWeighted average of the three experimental values. Error given is single standard deviation of intercept.

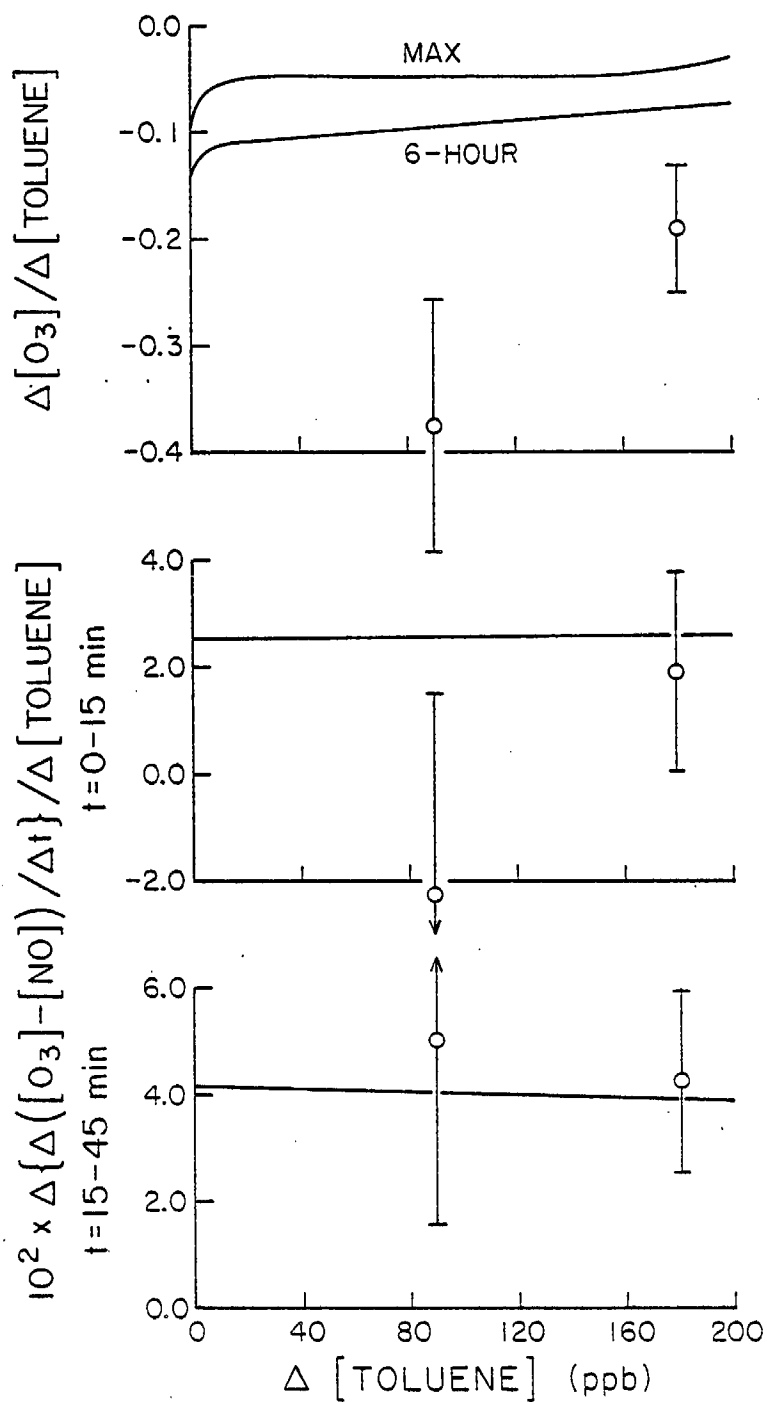


Figure IV-8a. Plots of the Experimental (O) and Calculated (-) Incremental Reactivities Against the Incremental Change in the Amount of Toluene in NO_x -Mini-Surrogate-Air Irradiations.

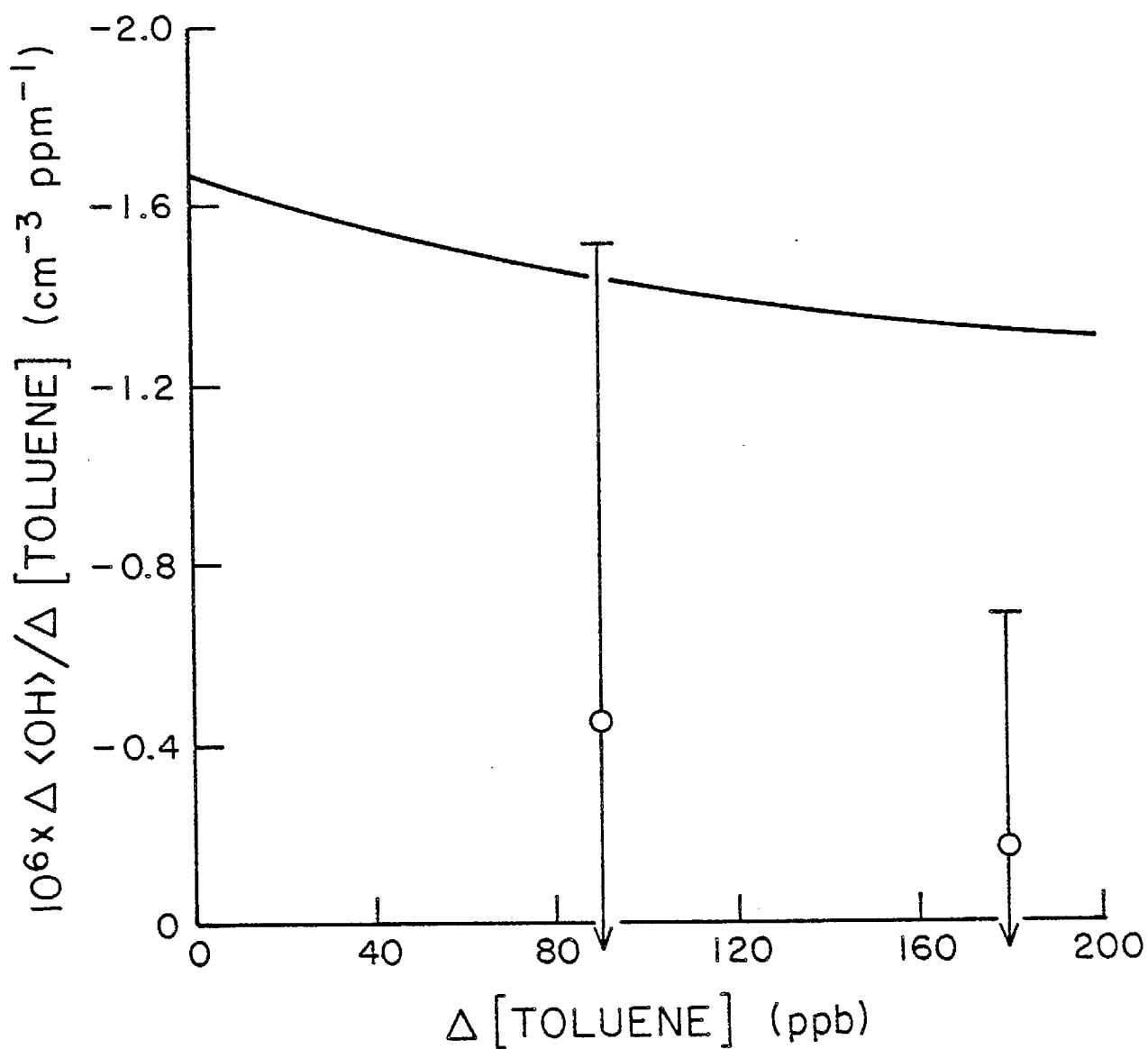


Figure IV-8b. Plot of the Experimental (O) and Calculated (-) Incremental Reactivities Against the Incremental Change in the Amount of Toluene in NO_x -Mini-Surrogate-Air Irradiations.

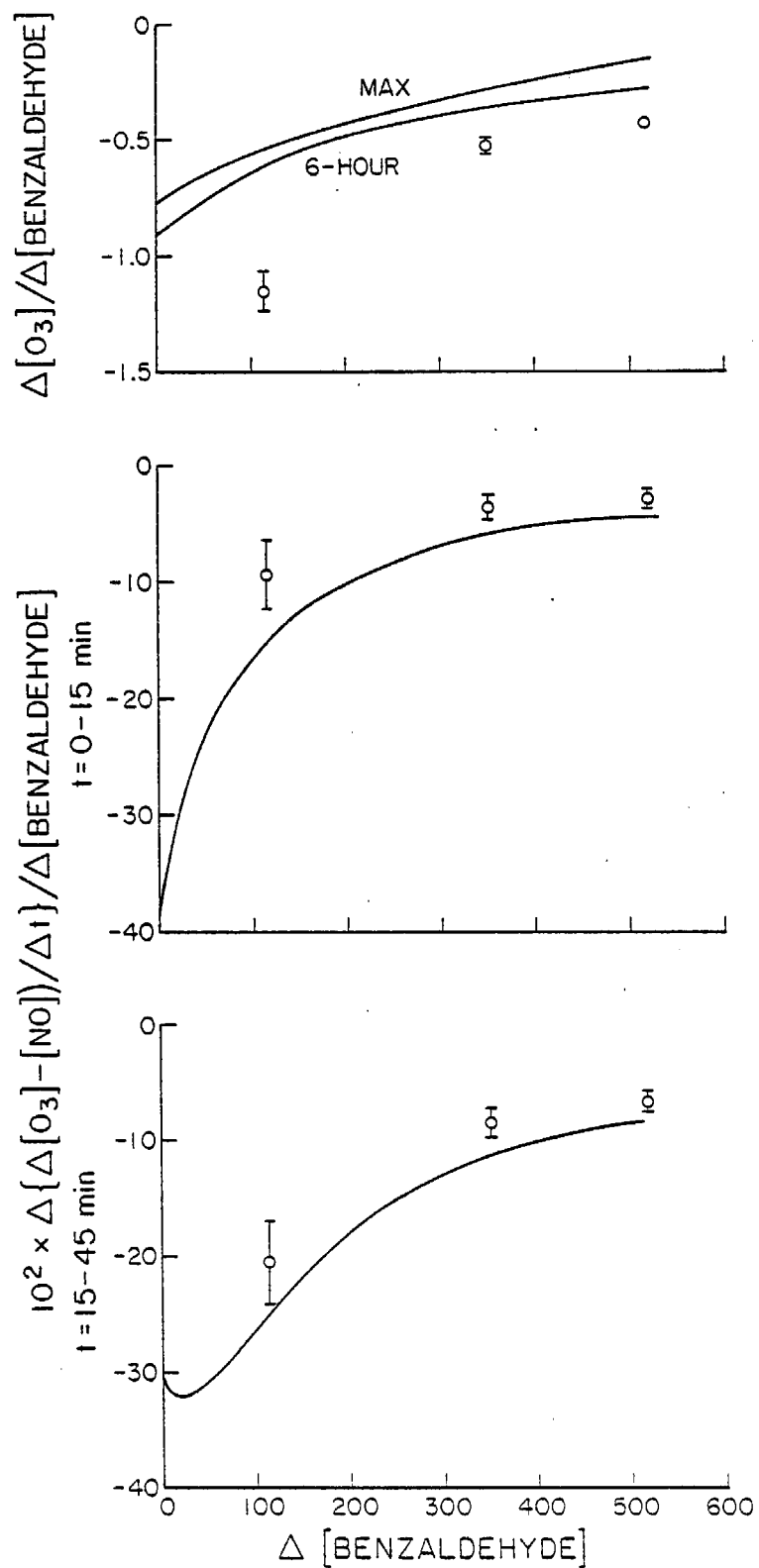


Figure IV-9a. Plots of the Experimental (O) and Calculated (-) Incremental Reactivities Against the Incremental Change in the Amount of Benzaldehyde in NO_x -Mini-Surrogate-Air Irradiations.

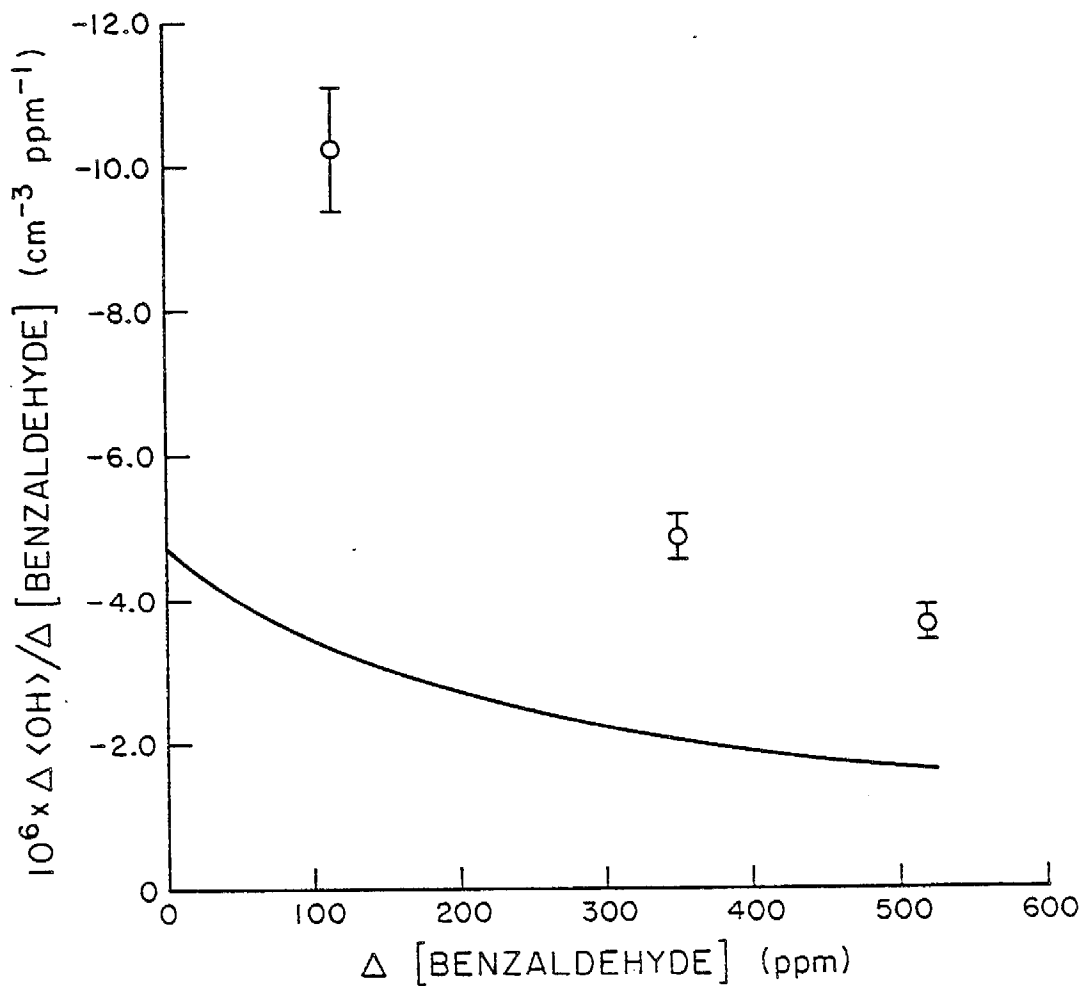


Figure IV-9b. Plots of the Experimental (O) and Calculated (-) Incremental Reactivities Against the Incremental Change in the Amount of Benzaldehyde in NO_x -Mini-Surrogate-Air Irradiations.

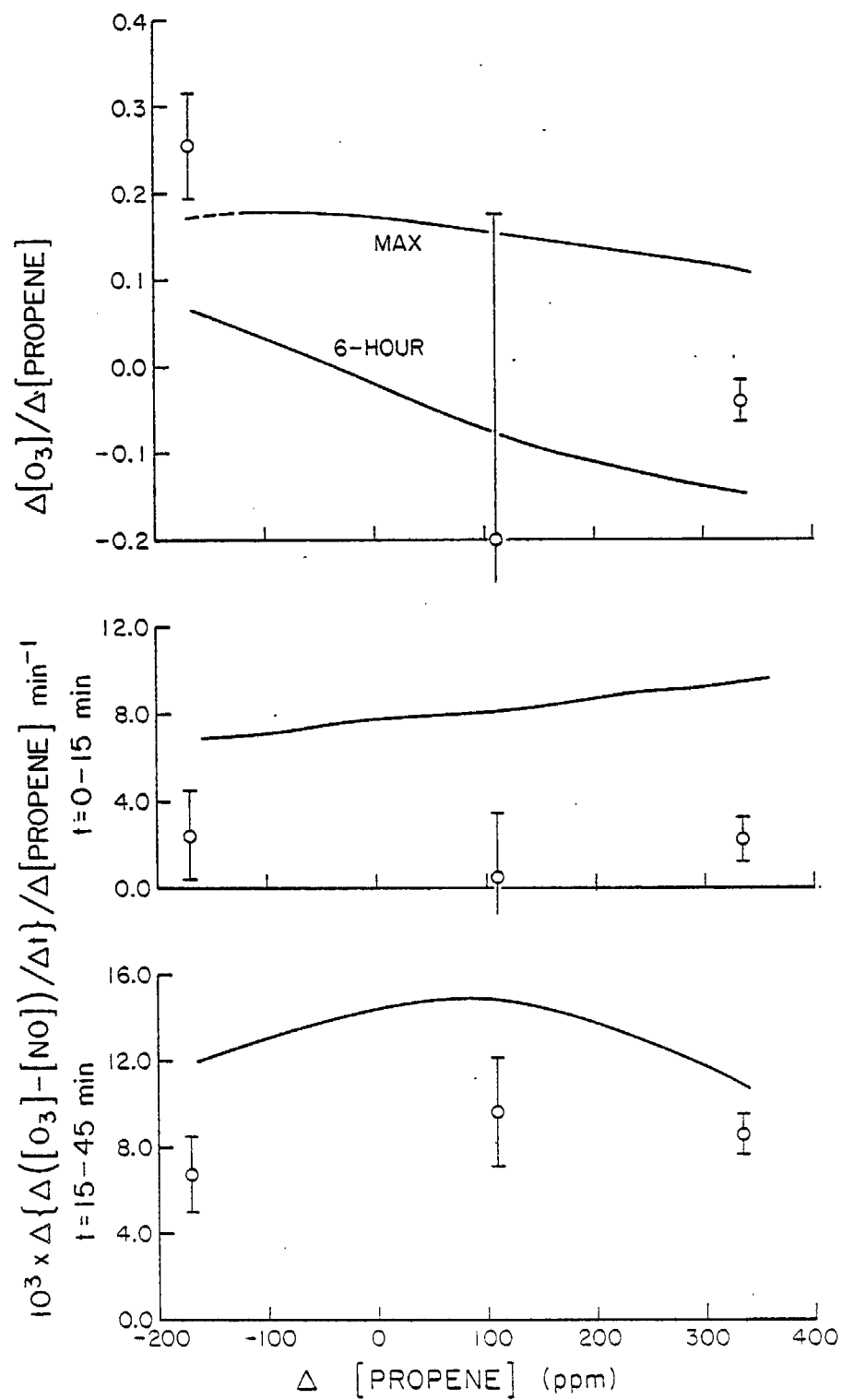


Figure IV-10a. Plots of the Experimental (O) and Calculated (-) Incremental Reactivities Against the Incremental Change in the Amount of Propene in NO_x -Mini-Surrogate-Air Irradiations.

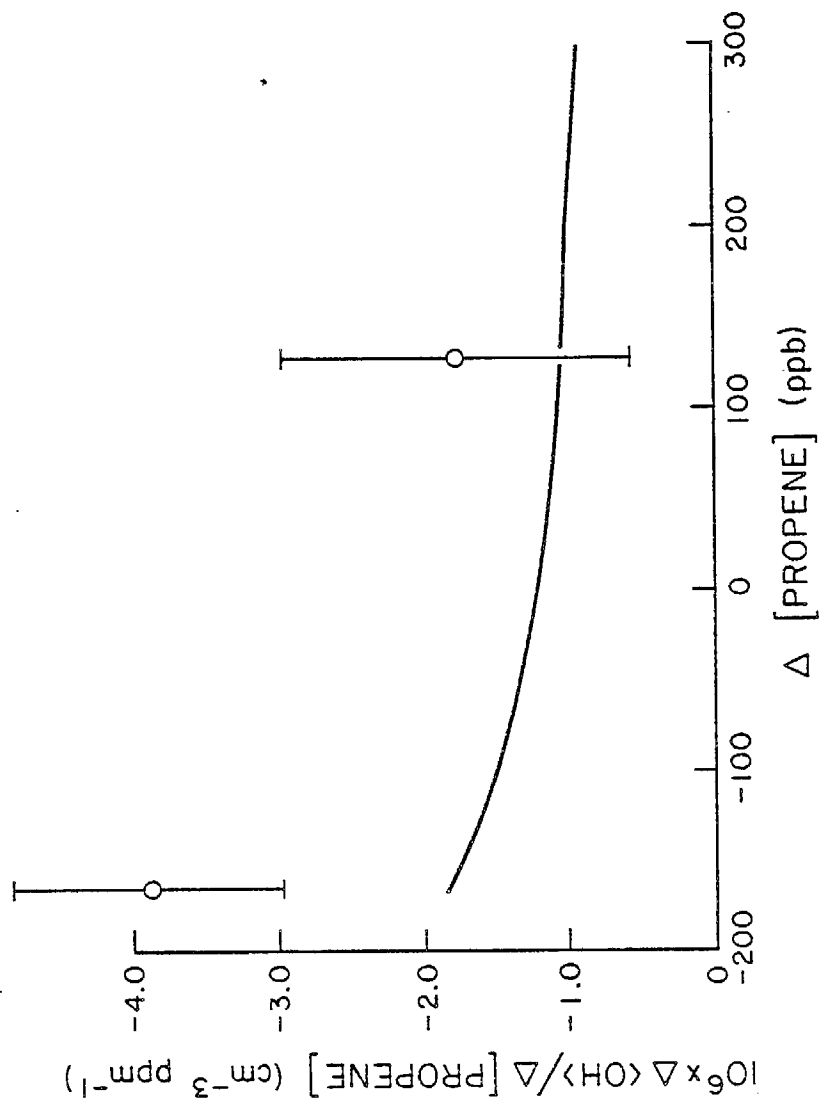


Figure IV-10b. Plots of the Experimental (O) and Calculated (-) Incremental Reactivities Against the Incremental Change in the Amount of Propene in NO_x -Mini-Surrogate-Air Irradiations.

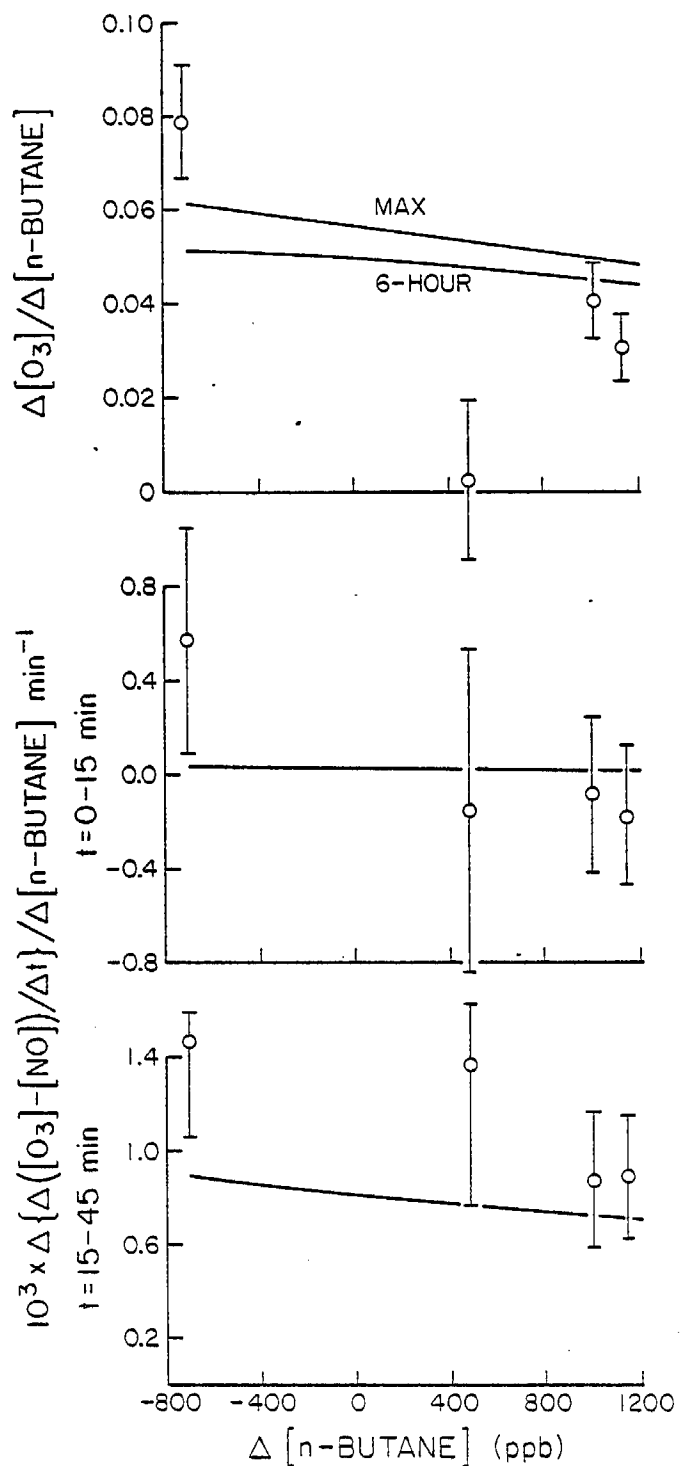


Figure IV-11a. Plots of the Experimental (O) and Calculated (-) Incremental Reactivities Against the Incremental Change in the Amount of n-Butane in NO_x -Mini-Surrogate-Air Irradiations.

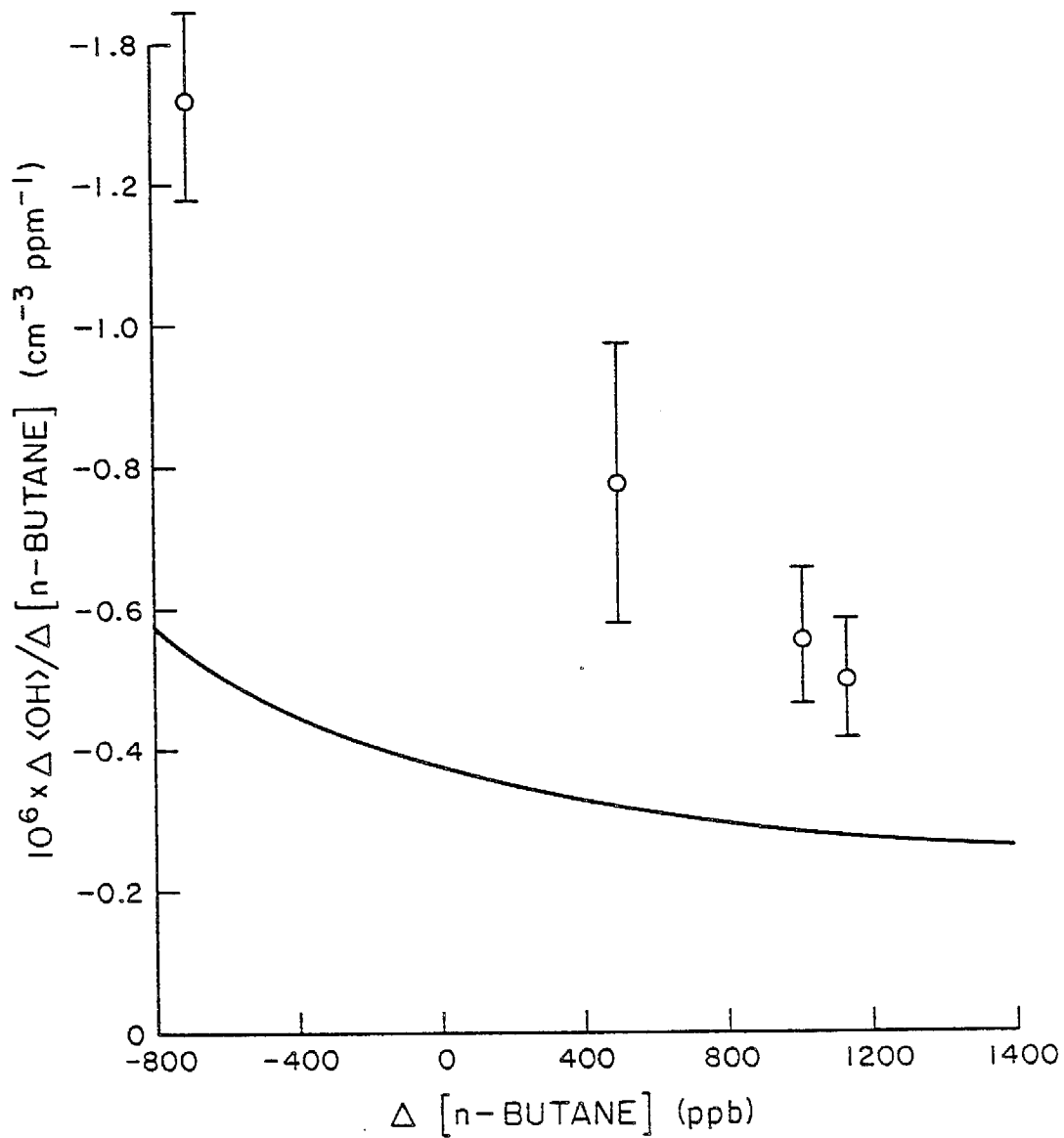


Figure IV-11b. Plots of the Experimental (O) and Calculated (-) Incremental Reactivities Against the Incremental Change in the Amount of n-Butane in NO_x -Mini-Surrogate-Air Irradiations.

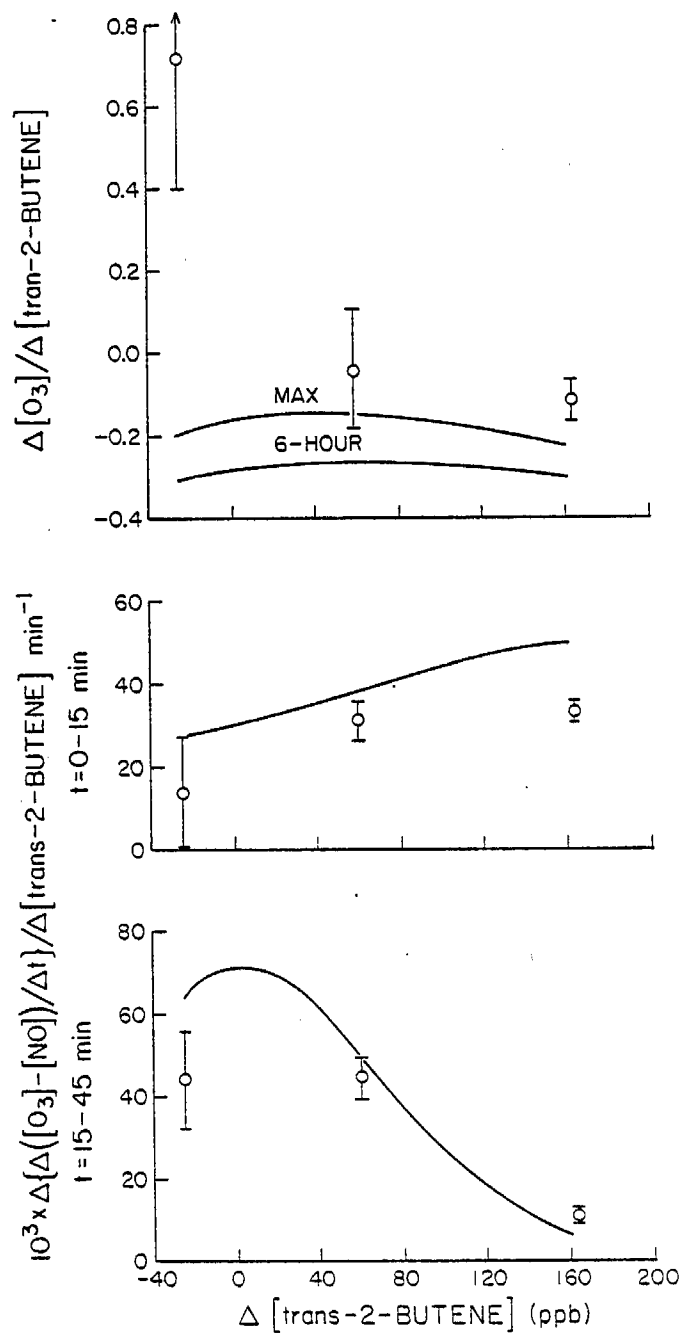


Figure IV-12a. Plots of the Experimental (O) and Calculated (-) Incremental Reactivities Against the Incremental Change in the Amount of trans-2-Butene in NO_x -Mini-Surrogate-Air Irradiations.

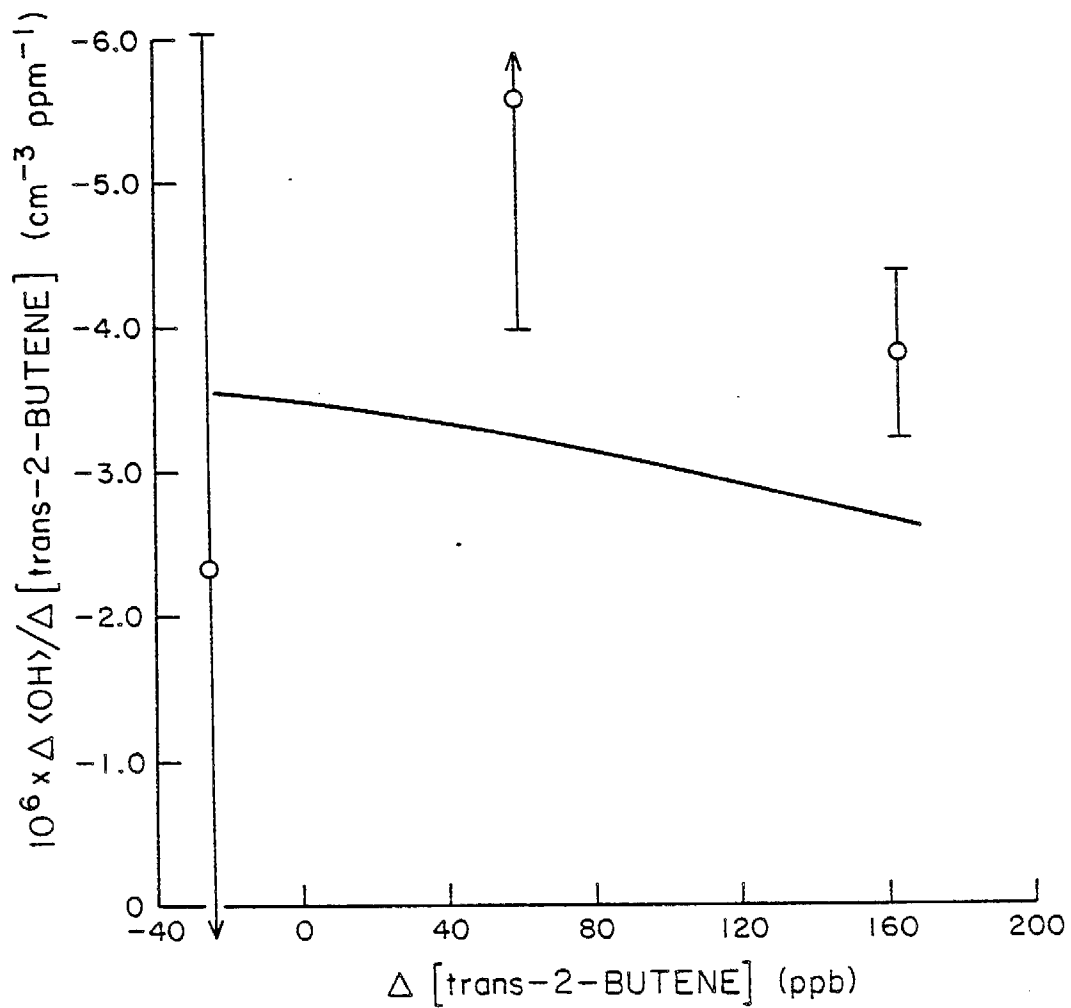


Figure IV-12b. Plots of the Experimental (O) and Calculated (-) Incremental Reactivities Against the Incremental Change in the Amount of trans-2-Butene in NO_x -Mini-Surrogate-Air Irradiations.

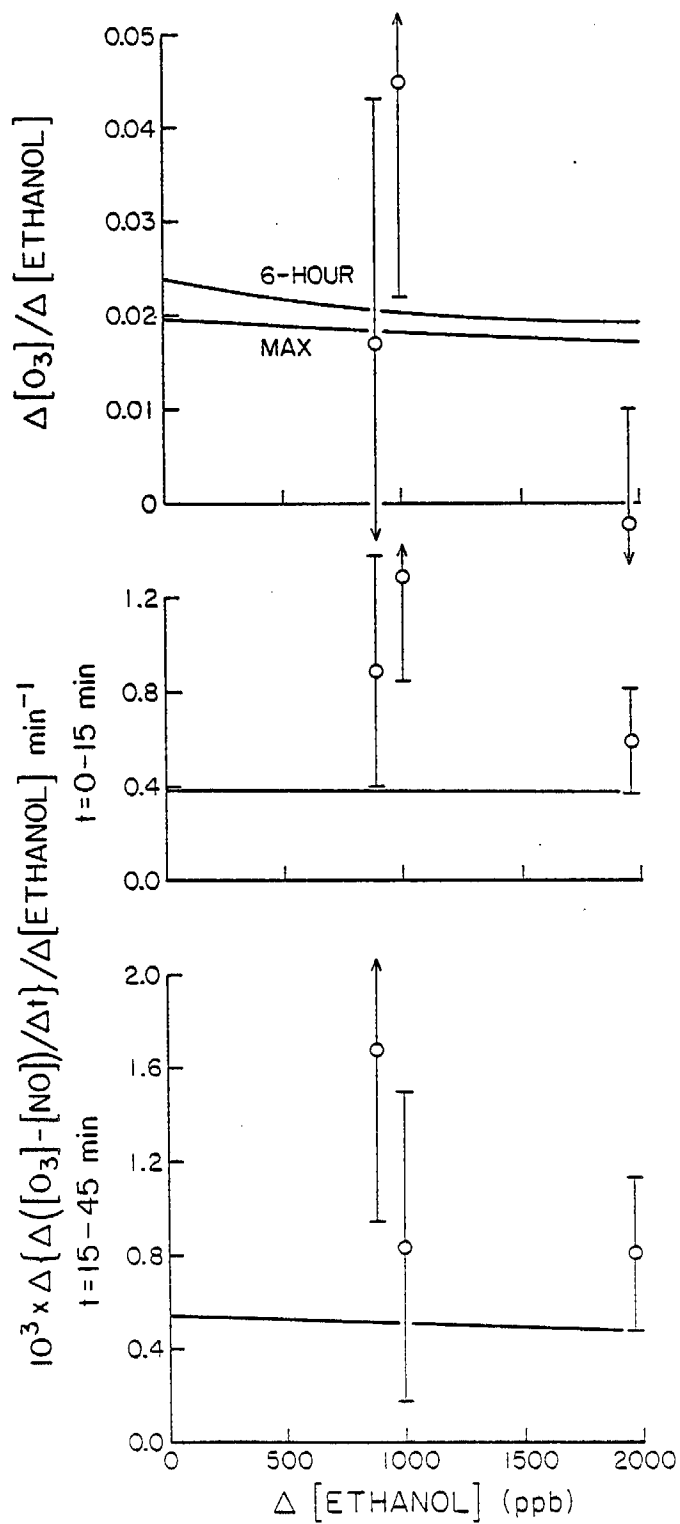


Figure IV-13a. Plots of the Experimental (O) and Calculated (-) Incremental Reactivities Against the Incremental Change in the Amount of Ethanol in NO_x -Mini-Surrogate-Air Irradiations.

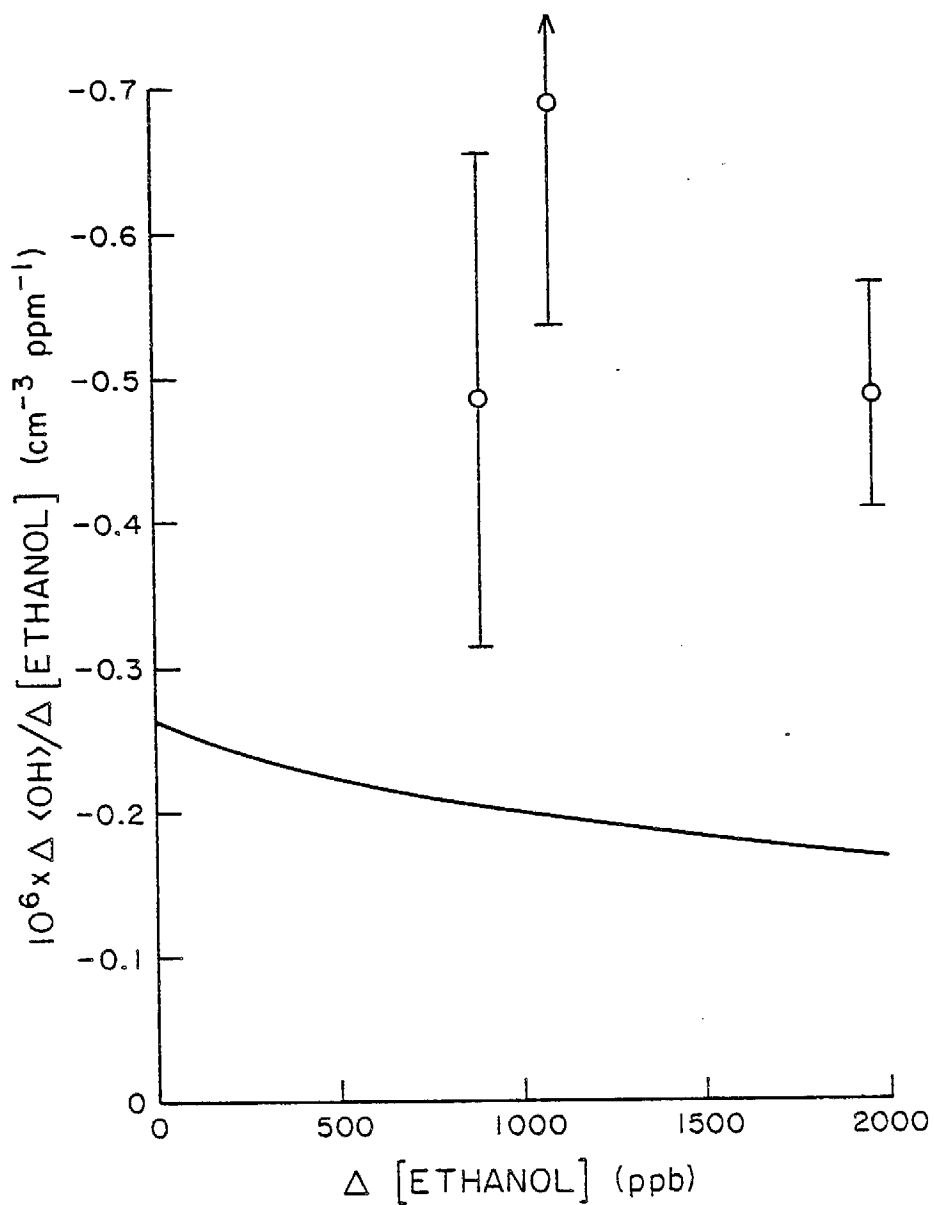


Figure IV-13b. Plots of the Experimental (O) and Calculated (-) Incremental Reactivities Against the Incremental Change in the Amount of Ethanol in NO_x -Mini-Surrogate-Air Irradiations.

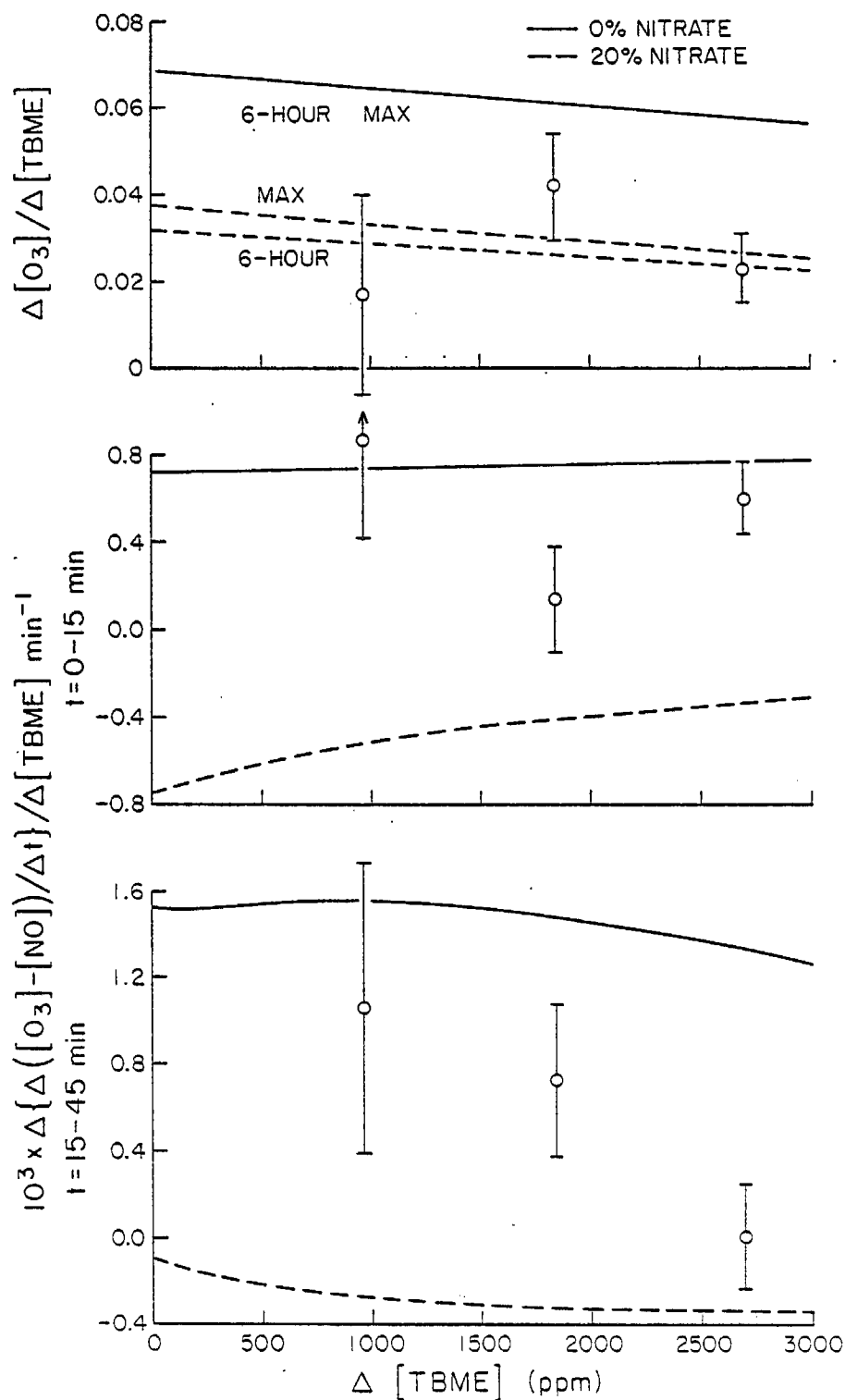


Figure IV-14a. Plots of the Experimental (O) and Calculated (-) Incremental Reactivities Against the Incremental Change in the Amount of tert.-Butyl Methyl Ether in NO_x -Mini-Surrogate-Air Irradiations. The Solid Lines are Calculations with 0% Alkyl Nitrate Formation, the Dashed Lines are for Calculations with 20% Alkyl Nitrate Formation (See Text).

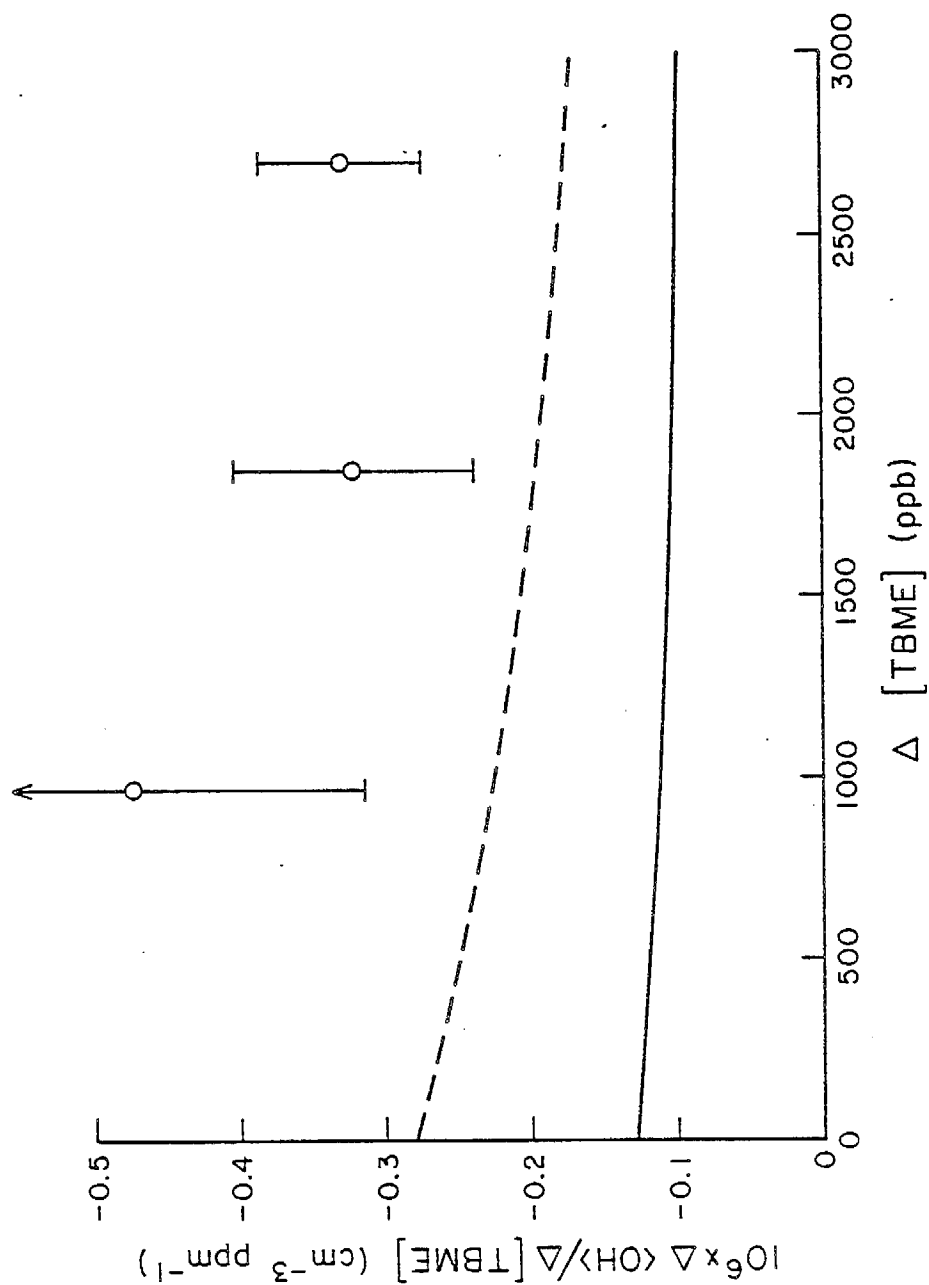


Figure IV-14b. Plots of the Experimental (O) and Calculated (—) Incremental Reactivities Against the Incremental Change in the Amount of tert.-Butyl Methyl Ether in NO -Mini-Surrogate-Air Irradiations. The Solid Line is the Calculations with 0% Alkyl Nitrate Formation, the Dashed Line is for 20% Alkyl Nitrate Formation (See Text).

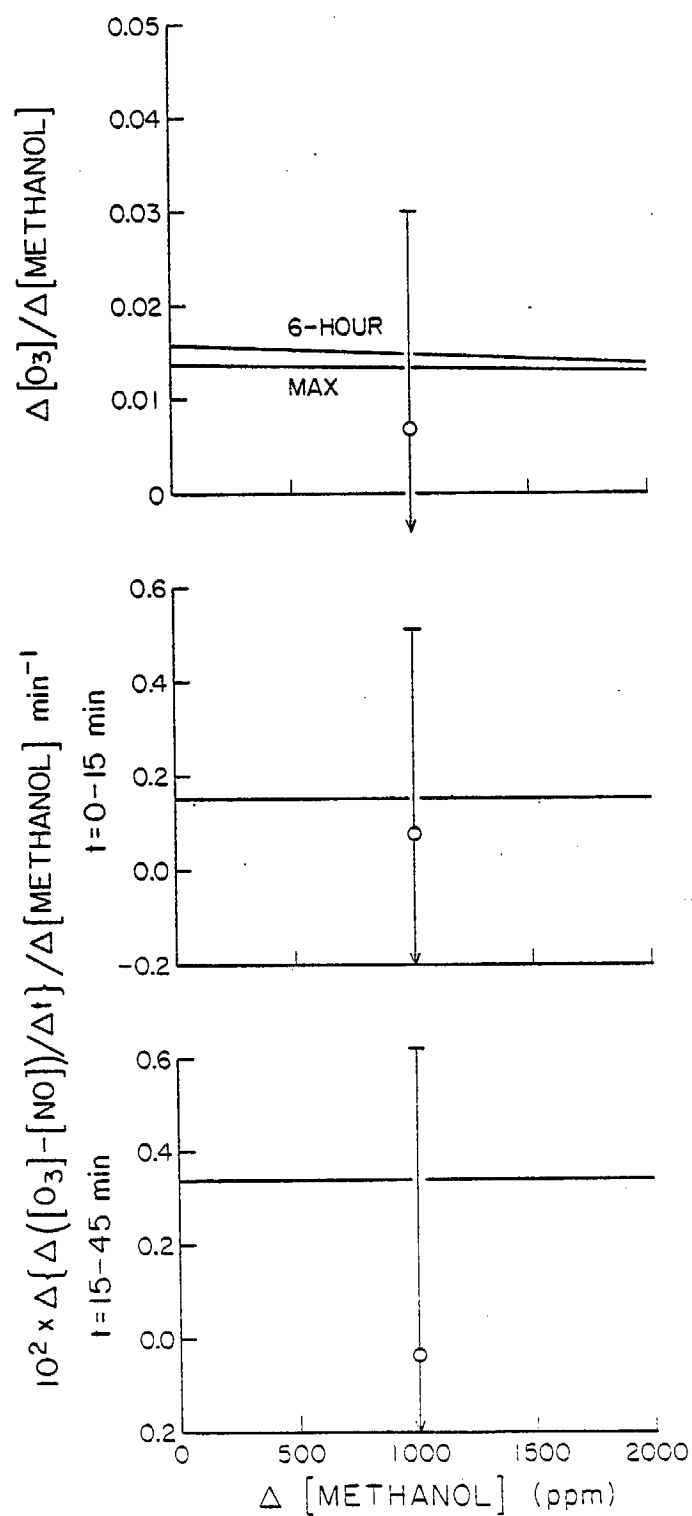


Figure IV-15a. Plots of the Experimental (O) and Calculated (-) Incremental Reactivities Against the Incremental Change in the Amount of Methanol in NO_x -Mini-Surrogate-Air Irradiations.

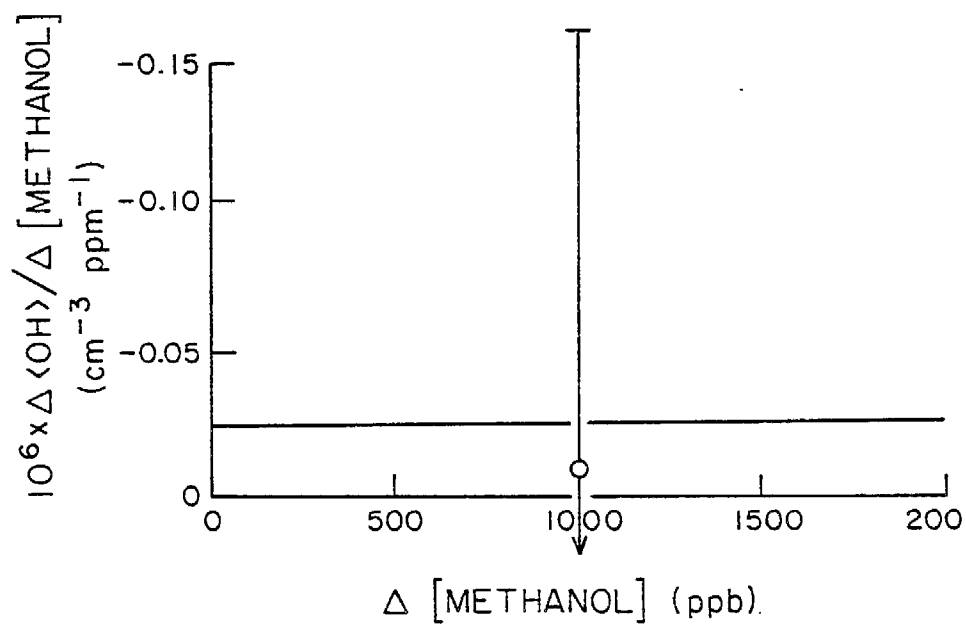


Figure IV-15b. Plots of the Experimental (O) and Calculated (-) Incremental Reactivities Against the Incremental Change in the Amount of Methanol in NO_x -Mini-Surrogate-Air Irradiations.

limiting incremental reactivity values, estimated either by weighted averages of the $I_R^{\Delta[\text{organic}]}$ values or by weighted linear least squares regression of $I_R^{\Delta[\text{organic}]}$ against $\Delta[\text{organic}]$, are summarized in Table IV-7 (given in brackets above the $I_R^{\Delta[\text{organic}]}$ values from which they were derived), along with an indication of the estimation method used.

D. Computer Model Calculations of Incremental Reactivity Values

In order to determine whether the experimental incremental reactivity values derived as discussed in the previous section are reasonably consistent with our current understanding of the chemistry of organic- NO_x -air irradiations, and in order to evaluate the dependence of the change of reactivity on the magnitude of amount of test organic added, a computer modeling study of the irradiations discussed in the previous section was carried out. In particular, a chemical kinetic computer model for the NO_x -air photooxidations of the components of the mini-surrogate and the five other test organics employed in our experimental studies, incorporating provisions for chamber effects appropriate for the SAPRC all-Teflon chamber under the conditions of these experiments, was employed to calculate the changes of reactivity caused by incremental addition and removal of the eight different test organics studied. Theoretical predictions of $I_R^{\Delta[\text{organic}]}$ as a function of $\Delta[\text{organic}]$, and of the limiting incremental reactivity values, I_R^0 were derived from this chemical kinetic computer study. In this section, the chemical model employed is briefly discussed, and the theoretical predictions are presented and compared with the experimental values.

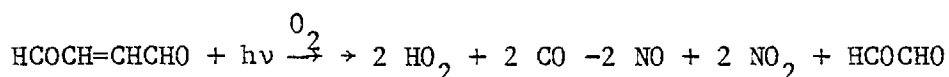
Reaction mechanisms. The chemical models employed in this study for n-butane, propene, trans-2-butene and benzaldehyde were identical to those recently published by Atkinson et al. (1982a), and thus need not be discussed further here. For the aromatics toluene and m-xylene, the recent data of Plum et al. (1983) [described in our final report to the California Air Resources Board Contract No. Al-030-32, Pitts et al. (1983)] dealing with the chemistry of the α -dicarbonyls shows that the chemical models of Atkinson et al. (1980, 1982a) are incorrect in that they assumed that methylglyoxal photolysis had a quantum yield of 1.0 in its $\lambda = 350\text{--}500$ nm absorption band, whereas Plum et al. measured the overall quantum yield for that wavelength region to be only 0.18. This is a

significant discrepancy, since methylglyoxal photolysis is assumed to be the major radical source in the photooxidation of these aromatics. If the overall experimental quantum yield of Plum et al. (1983) is incorporated into the otherwise unmodified models of Atkinson et al. (1980, 1982a), then the model significantly underpredicts the reactivities observed in toluene-NO_x-air (Atkinson et al. 1980, Pitts et al. 1979) and m-xylene-NO_x-air (Pitts et al. 1979) chamber irradiations. The modified aromatics model employed in this study will be discussed in more detail elsewhere (Carter et al. 1983). Briefly, in order to fit our very recent experimental chamber data for benzene-NO_x-air (Pitts et al. 1983) as well as our previous toluene-NO_x-air (Atkinson et al. 1982) and m-xylene-NO_x-air (Pitts et al. 1979) data, the following modifications were made to the model of Atkinson et al. (1982a):

(1) The absorption coefficients and quantum yields for glyoxal and methylglyoxal photolysis measured by Plum et al. (1983) were used. The mechanisms of those photolysis reactions were not changed.

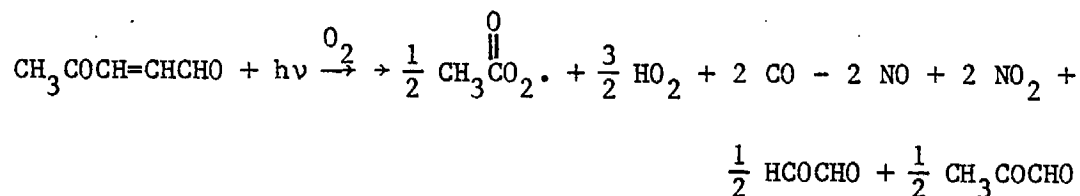
(2) The formation of alkyl nitrates from the reactions of NO with the various peroxy radicals formed in the aromatic photooxidation reactions was assumed to be negligible, in contrast with the model of Atkinson et al. (1980), which had alkyl nitrate formation occurring 25% of the time from these reactions [based on analogy with reactions of peroxy radicals formed from the n-alkanes (Darnall et al. 1976b, Atkinson et al. 1982b)]. This change increases the predicted reactivity in aromatic-NO_x irradiations, but not by enough to compensate for the loss of reactivity caused by reducing the α-dicarbonyl quantum yields.

(3) As discussed in our final report to the California Air Resources Board Contract No. A1-030-32 (Pitts et al. 1983), our recent benzene-NO_x-air environmental chamber data cannot be satisfactorily fit by model calculations unless it is assumed that 2-butene-1,4-dial, which is also assumed to be formed in the toluene system (Atkinson et al. 1980, 1982a), photolyzes to form radical species via the overall reaction



at a rate ~0.0065 times that of the photolysis of NO₂.

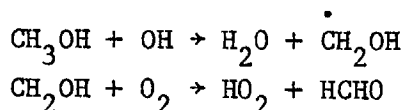
(4) In order to simulate the relatively high reactivity observed in m-xylene-NO_x-air chamber irradiations (Pitts et al. 1979), an analogous adjustment of the photolysis of 2-pentene 1,4-dial, assumed to be formed in both the m-xylene and the toluene systems (Atkinson et al. 1982a), to radicals was made.



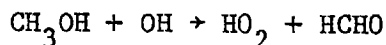
The m-xylene-NO_x-air data (Pitts et al. 1979) were best fit by assuming that this dicarbonyl photolyzes at a rate which is 0.03 times that of the photolysis of NO₂.

Although there are no published validated mechanisms for the NO_x-air photooxidations of methanol and ethanol, their reaction mechanisms appear to be relatively straightforward. Both are believed to be consumed primarily by reaction with hydroxyl radicals, and the results of product studies by Carter et al. (1979a) and Niki et al. (1978) indicate that the reactions proceed as shown below:

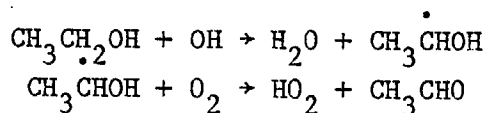
for methanol



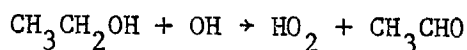
or overall:



and for ethanol

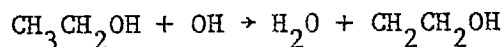


or overall:



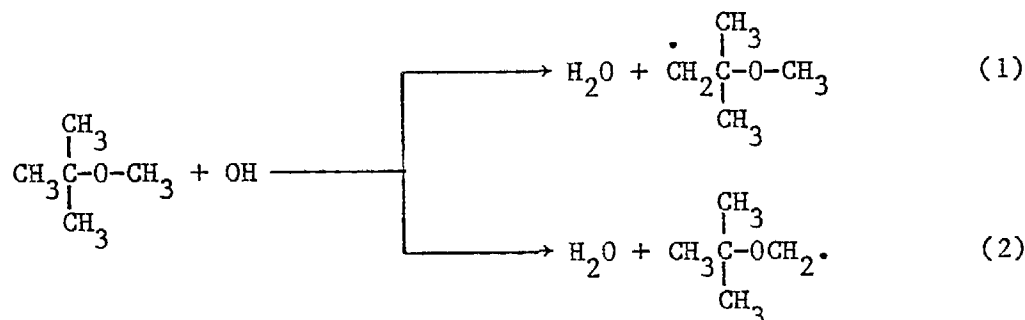
The rate constants for the reaction of OH radicals with methanol and ethanol have been measured to be 1.0×10^{-12} cm³ molecule⁻¹ sec⁻¹ and 3.5

$\times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$, respectively, at room temperature (Atkinson et al. 1979). Based on the product data of Carter et al. (1979a) and kinetic estimates (Atkinson et al. 1979), the alternate reaction pathway for ethanol



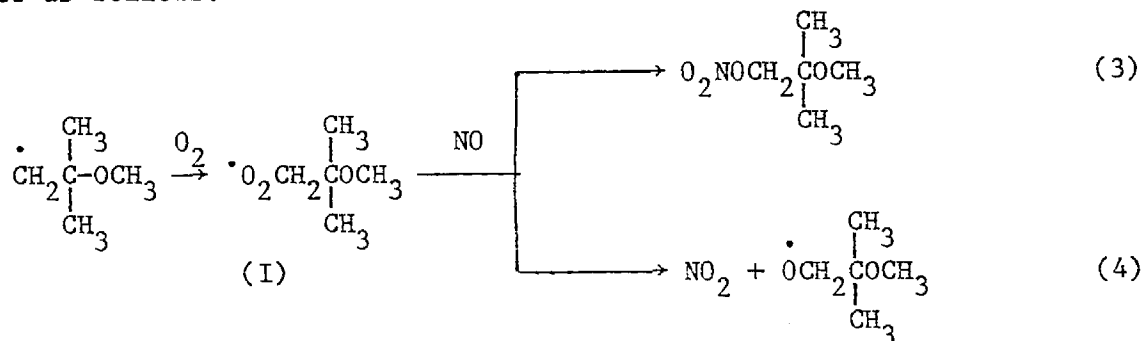
is assumed to occur <10-15% of the time, and has been ignored in this modeling study.

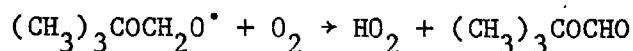
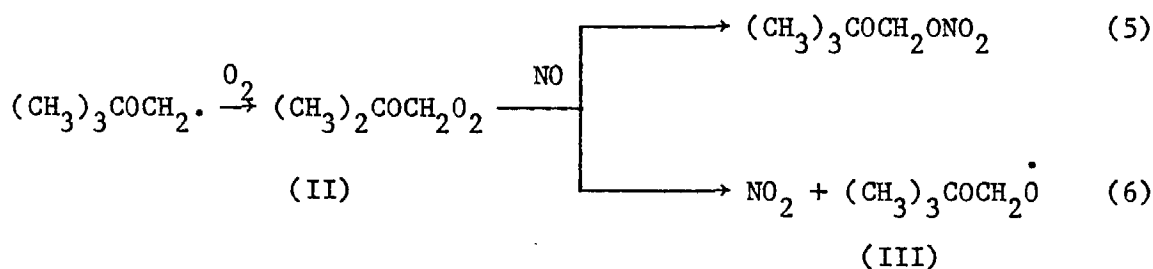
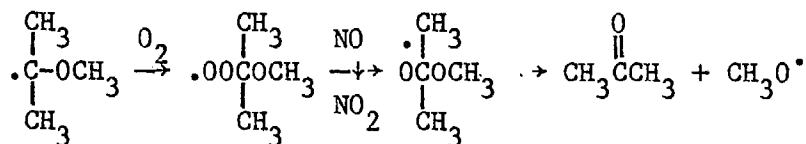
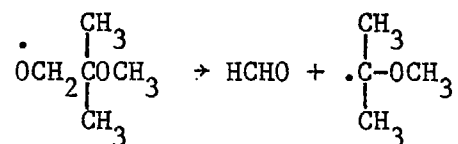
The mechanism for the photooxidation of t-butyl methyl ether (TBME) is somewhat more uncertain. It is assumed to be consumed primarily by reaction with hydroxyl radicals, and two modes of reactions are possible:



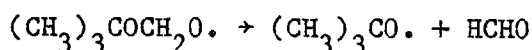
The total rate constant for the reaction of OH radicals with TBME at room temperature has been measured to be $2.5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ (Cox and Goldstone 1982). Based on kinetic data for reactions of OH + alkanes (Atkinson et al. 1979), it is estimated that OH abstracts from a primary C-H bond at a rate constant of $\sim 6 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ per bond, from which we estimate $k_1 = 5.7 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1}$; which, when combined with the experimental value of $k_1 + k_2$, gives $k_2 = 1.9 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$.

The radicals formed in the initial OH + TBME reaction are assumed to react as follows:





The competing decomposition of (III)

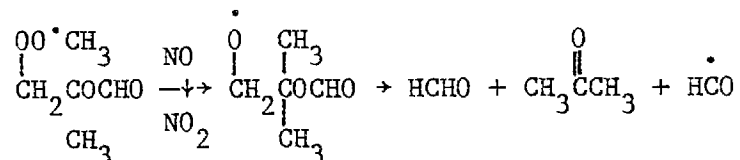
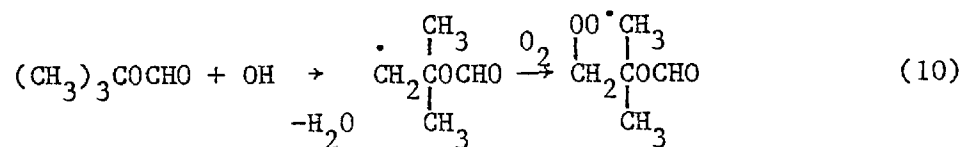
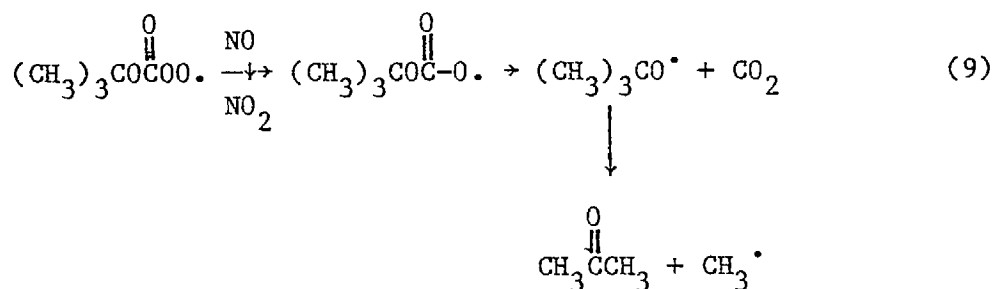
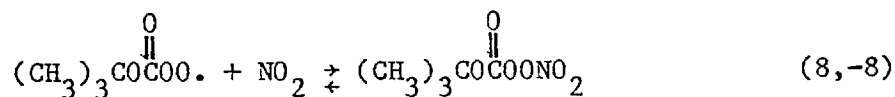
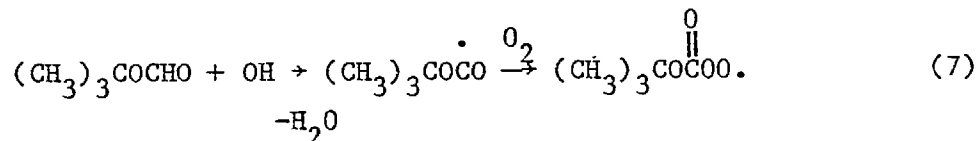


is assumed to be negligible, based on the recent work of Tuazon et al. (1983), where methyl formate was observed to be the sole photooxidation product of the NO_x -air photooxidation of dimethyl ether.

The rate constant ratios $k_3/(k_3 + k_4)$ and $k_5/(k_5 + k_6)$ [i.e., the efficiency of nitrate formation from the initially formed peroxy radicals (I) and (II)], are not known, but for the radicals formed from the n-alkanes it increases with the size of the molecule, ranging from ~0 for C_1 - C_2 peroxy radicals to ~0.35-0.40 for $\geq \text{C}_8$ species (Atkinson et al. 1982b). For the purpose of this work, two sets of calculations were

carried out: one assuming that, $k_3/(k_3 + k_4) = k_5/(k_5 + k_6) = 0$, and the other assuming that $k_3/(k_3 + k_4) = k_5/(k_5 + k_6) = 0.2$, the latter based on the nitrate yields observed in the n-pentane system (Atkinson et al. 1982b).

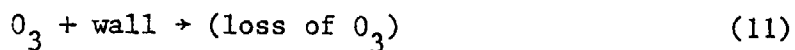
The secondary reactions of the major product, t-butyl formate, were also included in the TBME-NO_x photooxidation mechanism:



It was assumed that, based on the known OH + methyl formate rate constant (Tuazon et al. 1983), $k_7 = 2.5 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$, and a value of $k_{10} = 5.7 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ was assumed based on the rates of abstraction from primary C-H bonds in alkanes (Atkinson et al. 1979). It was also assumed that the values of k_8 , k_{-8} , and k_9 were the same as those for the analogous reactions of acetylperoxy radicals and acetylperoxy nitrate (Atkinson and Lloyd, 1983).

Chamber-Dependent Reactions. The rates of photolysis reactions and surface-dependent reactions appropriate for the indoor Teflon chamber with 70% blacklight irradiation were employed in the model simulations. The rates of the photolysis reactions were calculated using the absorption coefficients and quantum yields recommended by Atkinson and Lloyd (1983) or, for the α -dicarbonyls, of Plum et al. (1983), using the measured relative spectral distribution of the blacklights, normalized to the measured k_1 values. Since the k_1 values varied throughout this series of experiments (see Figure IV-4), the k_1 value employed in calculating the change of reactivity caused by varying levels of a given test organic was that appropriate for the time of the experiments in which that test organic was varied. For example, in calculating the reactivity effects for toluene which was studied in runs ITC 451-455, a value of $k_1 = 0.315 \text{ min}^{-1}$ was employed, while in calculating the effects for methanol, studied in run ITC 613, a value of $k_1 = 0.310 \text{ min}^{-1}$ was employed (see Figure IV-4). For propene, which was studied in two sets of runs (ITC 472-478 and ITC 479-585), $k_1 = 0.315 \text{ min}^{-1}$, appropriate for the second set of runs, was employed.

The model also included the following chamber-dependent reactions to represent heterogeneous effects:



Reaction (11) represents O_3 wall loss, and we used a value of $k_{11} = 8.3 \times 10^{-5} \text{ min}^{-1}$, based on the measured rates of O_3 dark decay in that

chamber. The rate of N_2O_5 hydrolysis (reaction 12) in Teflon bag chambers is unknown, and it was assumed to be slow ($k_{12} \approx 0$). Reaction (13) represents the chamber-dependent radical source discussed by Carter et al. (1982a). The rate of this reaction was measured by the tracer- NO_x -air irradiations which were conducted periodically during this program as discussed above. Based on the results of these experiments (see Table IV-6), we used a constant radical flux of $R_{13} = 0.06 \text{ ppb min}^{-1}$ for all of the chamber simulations reported here.

Results of calculations. The mechanism was tested by comparing its predictions against results of selected single and multi-hydrocarbon- NO_x -air runs conducted in the SAPRC evacuable chamber (Pitts et al. 1979, Atkinson et al. 1980) [using chamber effects appropriate for that chamber - as employed by Carter et al. (1979b) and Atkinson et al. (1980)] and against results of the standard mini-surrogate- NO_x runs conducted in this program. Fits to the evacuable chamber data were of comparable quality to those reported by Carter et al. (1979b), Atkinson et al. (1980), and Atkinson et al. (1982a), and were considered to be acceptable. A comparison of the model calculation to the results of several representative standard mini-surrogate- NO_x runs conducted in this program is shown in Figure IV-16. It can be seen that the model gives a reasonably good fit to the maximum O_3 yield, although it somewhat over-predicts the rate of O_3 formation and NO oxidation. The model also predicted that the O_3 reached a maximum and subsequently declined within the 6-hour period of the irradiation rather than leveling off or slowly increasing after its initial rapid formation, as was usually observed experimentally. However, for the purpose of assessing the effects of changes of composition of reactive organics, these discrepancies were not considered to be excessive, and no adjustment of the model was carried out to improve the fits.

Varying amounts of each of the eight test compounds studied in this program were then added to, or removed from, the mini-surrogate- NO_x mixture in the simulations, and the effects of these changes on maximum and 6-hour O_3 yields, 0-15 min and 15-45 min $\Delta([\text{O}_3]-[\text{NO}])/\Delta t$ values, and average OH radical concentrations were calculated. The calculated $\frac{\Delta[\text{organic}]}{I_R}$ values plotted against $\Delta[\text{organic}]$ for each of the test compounds are shown in Figures IV-8 through IV-15, where they can be

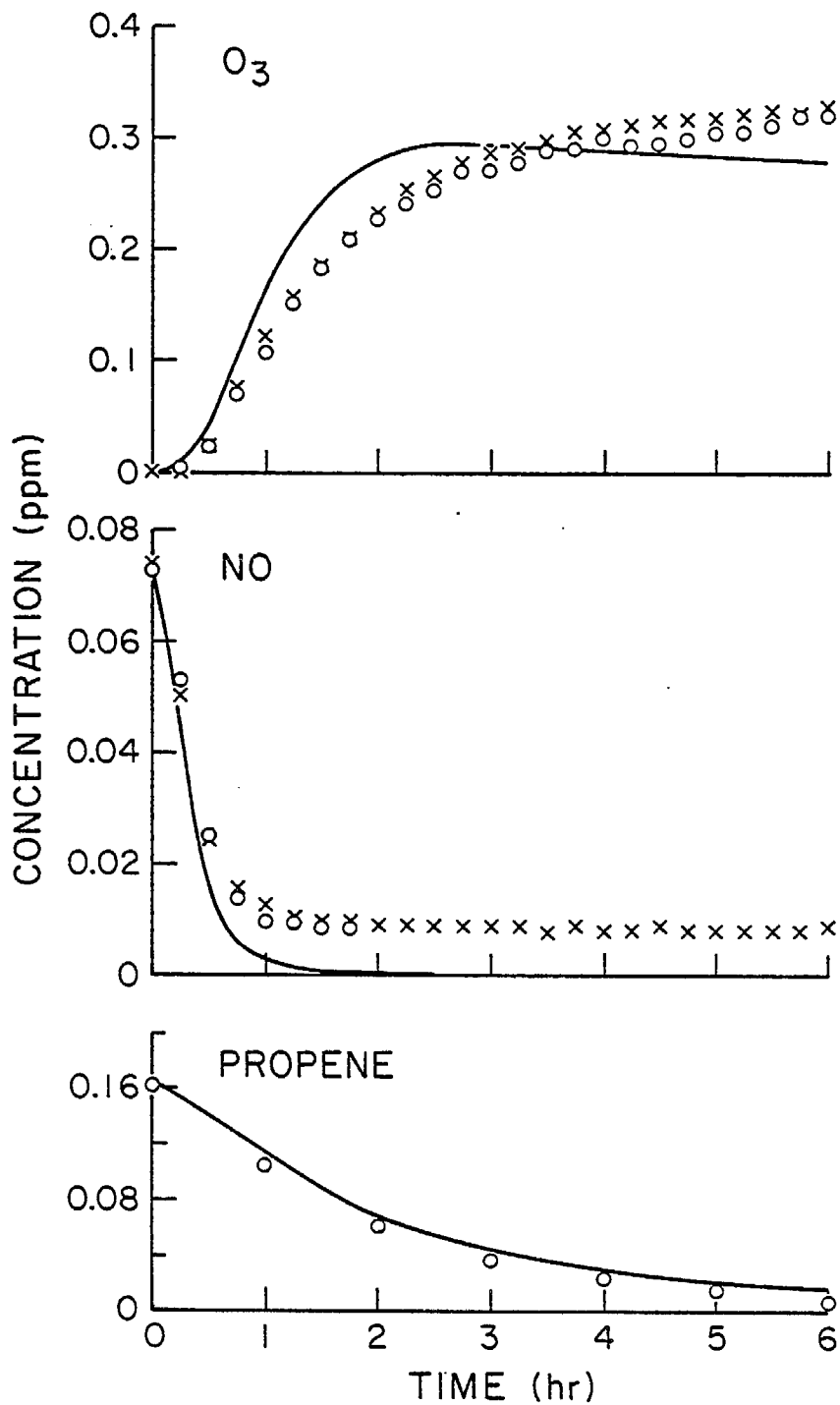


Figure IV-16. Comparison of Experimental (x-ITC 499, o-ITC 501) and Calculated (-) Time-Concentration Profiles for a Standard NO_x-Mini-Surrogate-Air Irradiation.

compared with the experimentally determined values. In addition, the calculated limiting incremental reactivity parameters, I_R^0 , are summarized in Table IV-8 for each reactivity measurement, where they can be compared with the experimental extrapolations.

It can be seen from the data in Figures IV-8 through IV-15 and Table IV-8 that in a number of cases the calculated curves fall outside the range of uncertainty estimated for the experimental data. In particular, except for toluene, the magnitude of the calculated $\Delta\langle OH \rangle / \Delta[\text{organic}]$ values are consistently lower than the experimental values for the compounds with sufficiently precise data for comparison. However, in most cases where the experimental data are sufficiently precise for meaningful comparison, the calculated shapes of the curves shown in Figures IV-8 through IV-15 are consistent with the experimental results, and the calculated and experimental incremental reactivity values generally agree in sign and approximate magnitude. These results are discussed in more detail in the following section.

Table IV-8. Summary of Observed^a and Calculated Limiting Incremental Reactivities for the Eight Organics Studied in this Program

Compound ^b	I _{max.} O ₃		I _Δ ([O ₃] - [NO])/Δt (10 ⁻³ min ⁻¹)				I _{<OH>} (10 ⁶ cm ⁻³ ppm ⁻¹)	
	Obs	Calc	t = 0-15 min		t = 15-45 min		Obs	Calc
			Obs	Calc	Obs	Calc		
Methanol	0.01 ± 0.02	0.014	0.1 ± 0.4	0.15	0 ± 0.7	0.34	0.01 ± 0.15	-0.03
t-Butyl methyl ether	0.028 ± 0.011	$\left\{ \begin{matrix} 0.069^c \\ 0.038^d \end{matrix} \right\}$	0.5 ± 0.3	$\left\{ \begin{matrix} 0.72^c \\ -0.74^d \end{matrix} \right\}$	0.3 ± 0.5	$\left\{ \begin{matrix} 1.52^c \\ -0.10^c \end{matrix} \right\}$	-0.34 ± 0.05	$\left\{ \begin{matrix} -0.13^c \\ -0.28^d \end{matrix} \right\}$
n-Butane	0.06 ± 0.01	0.056	0.3 ± 0.1	0.03	1.3 ± 0.1	0.80	-1.00 ± 0.01	-0.37
Ethanol	0.01 ± 0.02	0.024	0.8 ± 0.3	0.39	0.9 ± 0.4	0.55	-0.52 ± 0.09	-0.27
Toluene	-0.28 ± 0.13	-0.067	0 ± 3	2.6	4.6 ± 0.6	4.2	-0.3 ± 0.2	-1.6
Benzaldehyde	-1.0 ± 0.3	-0.77	-7 ± 3	-38.5	-17 ± 6	-30.8	-9 ± 2	-4.7
Propene	0.12 ± 0.05	0.175	3.2 ± 1.7	7.7	8.0 ± 0.8	14.4	-3.1 ± 0.2	-1.23
trans-2-Butene	0.2 ± 0.3	-0.16	33 ± 6	25.0	55 ± 10	71.5	-4.0 ± 0.8	-3.5

^afrom Table IV-7.

^bListed in order of increasing OH radical rate constant.

^cCalculated assuming no alkyl nitrate formation from the reaction of NO with the peroxy radicals formed from TBME.

^dCalculated assuming 20% alkyl nitrate formation from the reaction of NO with the peroxy radicals formed from TBME.

V. DISCUSSION AND CONCLUSIONS

In this section, the incremental reactivities measured and calculated as described in the previous section are discussed in terms of the chemical factors which affect rates and yields of ozone formation in photochemical smog systems. In addition, the implications of the results of this program in terms of ranking hydrocarbon reactivities for control strategy purposes are indicated.

A. Factors Affecting Ozone Formation

Although the reaction mechanisms of different types of hydrocarbons in NO_x -air irradiations can be complex and varied (see, for example Altshuller and Bufalini 1971, Demerjian et al. 1974, Finlayson-Pitts and Pitts 1977, Carter et al. 1979b, Atkinson et al. 1980, Atkinson and Lloyd 1983), for most organics ozone formation is influenced primarily by four major factors. The reactivity parameters measured in this program, specifically maximum O_3 yields, rates of change of $[\text{O}_3]$ - $[\text{NO}]$, and average hydroxyl radical levels, reflect to varying degrees these factors, which are indicated below:

(1) The rate at which the organic reacts in the atmosphere, particularly with OH radicals and, when applicable, by photolysis or reaction with O_3 or with the NO_3 radical, determines in part how fast the organic converts NO to NO_2 and thus how fast it causes O_3 formation.

(2) The number of molecules of NO oxidized per molecule of organic reacted determines how much O_3 will be formed by consumption of a given amount of the organic. This number is typically two to three for most organics whose photooxidation mechanisms have been studied (Washida et al. 1978, Cox et al. 1980), but can be larger for organics whose intermediate alkoxy radicals undergo extensive isomerization or fragmentation leading to other peroxy radicals whose corresponding alkoxy radicals also isomerize or fragment (Carter et al. 1979b, Whitten et al. 1979).

(3) For organics whose major atmospheric sink is reaction with hydroxyl radicals, the radical levels present also determines how fast the organic will cause O_3 formation. The photooxidation of some organics can result in increased radical levels, because either they or their major oxidation products undergo photolysis to form radicals. This enhancement

of radical levels causes the rates of O_3 formation from all organics present to be enhanced. On the other hand, certain organics can depress radical levels by converting radicals to intermediates which undergo termination reactions, and thus the presence of such compounds tends to reduce O_3 formation rates. For organics such as these, this tendency to depress or enhance radical levels can be an important aspect of their reactivity with respect to O_3 formation.

(4) Since O_3 formation can occur only as long as NO_x is present, organics whose atmospheric oxidation mechanism involves significant NO_x sinks will necessarily allow less O_3 formation under conditions when NO_x is limiting.

The rate at which an organic reacts in NO_x -air systems is obviously an important factor in influencing the reactivity of the organic since if it does not react at all, it will have no reactivity by any measurement. In addition, if the other three factors are the same, one would expect the rate at which the organic forms intermediates which oxidize NO and cause O_3 formation to be proportional, at least approximately, to the rate at which the organic reacts; and one would also expect that the extent to which the organic influences the final yield of ozone (or of any other product for that matter) would depend on how much of the initially present organic actually reacts, which obviously in turn depends on the rate at which it reacts.

In order to illustrate the extent to which the differences in atmospheric reaction rates of the organics studied in this program can account for the differences in some of the reactivity parameters observed, Table V-1 lists, for the eight organics studied in this program and a few other representative compounds, (a) the rate constant for the reaction of the organic with OH radicals (the major sink for most of these species), (b) the calculated fraction of the initially present organic which reacts in a 6-hour standard mini-surrogate- NO_x ITC run (calculated using the light intensity appropriate for the time the compound was studied) for the limit of $\Delta[\text{organic}] \rightarrow 0$, (c) the calculated incremental reactivity relative to O_3 yields, $I_{[O_3]_{\max}}^0$, divided by the fractional amount of the organic which reacts, and (d) the calculated incremental reactivity relative to the NO oxidation rate, $I_d^0([O_3]-[NO])/dt$ (specifically the average of the 0-15 minute and the 15-45 minute values), normalized by the OH + organic rate

Table V-1. Hydroxyl Radical Rate Constants, Calculated Fractions Reacted, and Normalized Calculated Incremental Reactivity Parameters for Selected Organics in Standard Mini-Surrogate-NO_x-Air Irradiations

Compound	$10^4 \times k_{OH}^a$ (ppm ⁻¹ min ⁻¹)	Fraction reacted ^b	$I_{[O_3]}^o$ max Fraction reacted ^c	$10^7 \times \frac{I_{\Delta([O_3]-[NO])/\Delta t}^o}{k_{OH}^d}$	$10^{-6} \times \frac{I_{<OH>}^o}{\text{Fraction reacted}}$ (cm ⁻³ ppm ⁻¹) ^e
Methanol	0.15	0.031	0.46	1.7	-1.0
t-Butyl methyl ether	0.36	0.072	$\begin{Bmatrix} 0.95^f \\ 0.53^g \end{Bmatrix}$	$\begin{Bmatrix} 3.1^f \\ -1.7^g \end{Bmatrix}$	$\begin{Bmatrix} -1.8^f \\ -3.8^g \end{Bmatrix}$
n-Butane	0.42	0.085	0.66	1.0	-4.4
Ethanol	0.46	0.091	0.26	1.0	-3.0
Toluene	0.89	0.179	-0.37	3.8	-8.9
Ethene	1.13	0.39	0.40	3.6	0.3
Formaldehyde	1.45	0.72	0.17	20.0	0.8
Benzaldehyde	1.89	0.78	-0.98	-18.4	-6.0
Acetaldehyde	2.28	0.41	-0.64	-2.6	-7.2
Propene	3.57	0.90	0.19	3.1	-1.5
trans-2-Butene	8.72	1.00	-0.16	5.5	-3.5

^aSee Section IV.D for references for OH + organic rate constants listed here. k_{OH} + ethene value from Atkinson and Lloyd (1983).

^bFraction of initially present organic which has reacted, at the limit of $\Delta[\text{organic}] \rightarrow 0$, during a six-hour standard mini-surrogate-NO_x-air irradiation, calculated using the same conditions as employed to calculate the I_R values.

^cCalculated $I_{[O_3]}^o$ values from Table IV-8.

^dAverage of the $t = 0-15$ and $t = 15-45$ minute limiting incremental reactivities for $\Delta([O_3]-[NO])/ \Delta t$ given in Table IV-8.

^eCalculated $I_{<OH>}^o$ values from Table IV-8.

^fCalculated assuming no nitrate formation from the reaction of NO with the peroxy radicals formed from TBME.

^gCalculated assuming 20% nitrate formation from the reaction of NO with the peroxy radicals formed from TBME.

constant. Calculated incremental reactivity values are used for comparison purposes; as discussed in Section IV.D, these are at least qualitatively consistent with the experimental values. It can be seen that normalizing these incremental reactivity parameters to account for differences in rates at which the organic reacts indeed decreases the range of variability of the reactivity parameters. However, significant differences still remain especially for the alkenes and the aromatics, clearly indicating that the rate at which the organic reacts cannot be the only factor of importance in determining reactivity. Furthermore, it should be noted that the present experimental and computer modeling study was carried out under essentially a single set of conditions with respect to the hydrocarbon/ NO_x ratio. For at least some of the organics studied, changes in the hydrocarbon/ NO_x ratio could lead to significant changes in their relative reactivities. This is expected to be especially true under NO_x -rich conditions (see below).

Perhaps the most significant manifestation of variability in the observed and calculated incremental reactivities relative to O_3 yields and NO oxidation rates is the fact that in some cases they differ not only in magnitude but also in sign - i.e., some compounds have "negative" reactivity. This effect, which obviously complicates control strategy considerations, can be explained mechanistically in terms of the effects of the photooxidation of the organic on radical levels and NO_x removal rates [factors (3) and (4) above], as is discussed below for the specific "negatively reactive" compounds studied in this program.

By far the most extreme example of negative reactivity of the compounds studied in this program is benzaldehyde. This is the most negative in terms of O_3 maximum yields (both before and after correction for the amount reacted), is the only compound with a large and unambiguous negative reactivity in terms of NO oxidation rates, and is also the most negative in terms of suppression of the average OH radical levels. This is not unexpected, since benzaldehyde is known from previous chamber studies to be a photochemical smog inhibitor (Kuntz et al. 1973; Gitchell et al. 1974), and its currently accepted photochemical mechanism, supported by modeling studies on environmental chamber data (Atkinson et al. 1980, Atkinson and Lloyd 1983), predicts that each reaction of benzaldehyde with hydroxyl radicals (its major atmospheric sink, along with

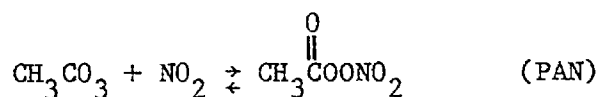
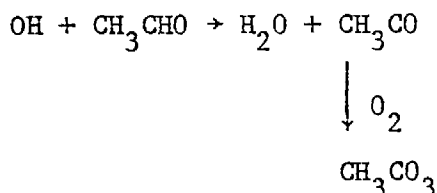
photolysis to form non-radical products) results in no radical regeneration (i.e., an 100% efficient radical sink), and also in the removal of at least one molecule of NO_x from the system (Atkinson et al. 1980). This contrasts with the other organics studied in this program, whose NO_x -air photooxidation mechanisms involve predominantly radical regeneration, and where NO_x sinks are primarily involved in secondary reactions of the products.

Toluene is interesting in that it is known to be a highly reactive compound in terms of O_3 formation when irradiated by itself in NO_x -air systems (Pitts et al. 1979). However, when added to the mini-surrogate mixture used here, it had a negative incremental reactivity in terms of the maximum O_3 yields, although it had a positive effect on NO oxidation rates. These observations can be explained by the presence of NO_x sinks in the toluene photooxidation mechanism which reduce the maximum O_3 yield. However, NO_x sinks do not significantly affect the initial NO oxidation rates, since there is no lack of NO_x during the initial stages of the irradiation, and NO oxidation rates are more sensitive to radical levels (as well as to the rate at which an organic reacts), and toluene, unlike benzaldehyde, is not believed to be a radical inhibitor. [Indeed, in order to fit model calculations to environmental chamber data, it is necessary to assume significant radical sources in the toluene photooxidation mechanisms (Atkinson et al. 1980).] The major NO_x sinks believed to occur in the photooxidation mechanism of toluene and other aromatic hydrocarbons include (Atkinson et al. 1980) the formation and reactions of benzaldehyde (see above), the formation of cresols and their subsequent rapid reaction with NO_3 (Carter et al. 1981), and the formation of methylglyoxal, which subsequently rapidly photolyzes (Plum et al. 1983) to form precursors to peroxyacetyl nitrate, which is an effective NO_x sink. The negative incremental reactivity of toluene with respect to O_3 formation and positive reactivity with respect to NO oxidation rates is reasonably well predicted by our model calculations (see Table IV-8 and Figure IV-8), indicating that the current aromatic mechanism adequately takes this effect into account.

The alkenes propene and trans-2-butene are analogous to toluene in that they have relatively high, positive incremental reactivity relative to NO oxidation rates, and yet have low or slightly negative incremental

reactivities with respect to O_3 yields. This could be due in part to the fact that these alkenes react directly with O_3 , although many of the intermediate species formed convert NO to NO_2 (or NO_2 to NO_3), which ultimately results in net O_3 formation (Atkinson and Lloyd 1983). Although the atmospheric photooxidation mechanism for the alkenes is quite different than that for the aromatics, they are similar in that their mechanisms involve both radical sources and NO_x sinks, which together account for the high, positive reactivity relative to NO oxidation rates, and low or negative incremental reactivity relative to O_3 maximum yields.

Both propene and trans-2-butene form acetaldehyde in high yields, which subsequently reacts to form PAN, the major NO_x sink in the photo-oxidation of these olefins. (Acetaldehyde itself is calculated to have a very negative effect on O_3 maxima, as can be seen in Table V-1).



As may be expected, ethene, which does not form acetaldehyde and is not expected to have significant NO_x sinks, is calculated to have a positive incremental reactivity relative to O_3 yields, after normalization for the amount of alkene consumed, considerably higher than those for propene and trans-2-butene (see Table V-1).

The alcohols methanol and ethanol both have positive incremental reactivities with respect to O_3 formation and NO oxidation rates, though they are significantly less reactive than toluene and the alkenes in the latter regard, even after normalization for the differences in reaction rates. This can be attributed to the fact that the photooxidation mechanisms for the alcohols lack the significant radical sources present in the aromatic and alkene photooxidations (i.e., photolysis of products for the aromatics, and reaction with O_3 for the alkenes). It can also be seen

from Table V-1 that the normalized incremental reactivity of methanol, relative to both O_3 yields and NO oxidation rates are both higher than that for ethanol. This can be attributed to the fact that ethanol forms acetaldehyde in its photooxidation mechanism, while methanol forms formaldehyde. As indicated above, acetaldehyde tends to act as a NO_x sink and thus reduce O_3 yields while formaldehyde does not. In addition, formaldehyde has a very high reactivity relative to NO oxidation rates, in contrast with acetaldehyde which is negatively reactive in this effect.

The high reactivity of formaldehyde with respect to NO oxidation rates can be attributed to radical production from its relatively rapid photolysis (Atkinson et al. 1983). Acetaldehyde photolyzes much less rapidly (Horowitz and Calvert 1982) and, as indicated above, reacts largely to form peroxyacetyl nitrate (PAN), a radical and NO_x sink. Indeed, when $[NO_2] \gg [NO]$, PAN formation is the only significant reaction pathway, making acetaldehyde analogous to benzaldehyde in that it is an effective radical and NO_x inhibitor. The fact that acetaldehyde is less negatively reactive than benzaldehyde arises because acetaldehyde photolyzes to some extent to form radicals, and when $[NO] \gtrsim [NO_2]$, reaction pathways other than PAN formation are significant. Formaldehyde does not form stable peroxy nitrates in its photooxidation (Atkinson and Lloyd 1983), which is another reason it is much more reactive than the other aldehydes.

The results of the calculations on t-butyl methyl ether are interesting in that they illustrate the effect of differing assumptions concerning alkyl nitrate yields from the reactions of NO with the peroxy radicals initially formed in the TBME + OH reaction (see Section IV.D). It can be seen that assuming no alkyl nitrate formation results in relatively high calculated incremental reactivities after normalizing for its reaction rate or amount consumed (see Table V-1), whereas assuming 20% nitrate formation results in negative calculated incremental reactivities for TBME, both for the maximum O_3 yields and the NO oxidation rates. Although the actual nitrate yields from the reactions of NO with the peroxy radicals formed from TBME are unknown, the data obviously indicate that it is somewhere between the values of 0% and 20% values assumed in the calculations (see Figure IV-14).

Table V-1 also summarizes the calculated limiting incremental values relative to average hydroxyl radical levels, normalized by the fraction of the organic which reacts. It can be seen that with the exception of formaldehyde and ethene all the compounds listed tend to reduce the average radical levels. This is caused by a combination of factors: Some organics tend to suppress radical levels directly by having radical sink processes in their photooxidation mechanisms, whereas others tend to remove NO_x from the system, which increases the amount of time in the 6-hour simulations when NO_x is absent from the system. This latter effect causes lower average hydroxyl radical levels because termination by radical + radical reactions become important when NO_x is not present. Radical initiation caused by the relatively rapid photolysis of formaldehyde (which is the major product formed from ethylene) is apparently more than enough to offset this effect, especially since formaldehyde has no radical or NO_x sinks in its photooxidation mechanism. Methanol is the only other compound of those listed in Table V-1 without radical or NO_x sinks, and indeed it has a relatively small effect on the average hydroxyl radical levels.

B. Summary and Conclusions

As noted in the introduction, any quantitative reactivity ranking of hydrocarbons will depend on the particular criterion adopted. Examples of criteria which have been employed in the past include ozone yields and dosages or NO to NO_2 conversion rates in single hydrocarbon- NO_x irradiations, hydrocarbon consumption rates, eye irritation indices, and reactivity of the hydrocarbon towards the hydroxyl (OH) radical. Additional criteria which could also be considered include aerosol formation rates and formation of toxic, mutagenic, or carcinogenic products. An alternate approach, which has not been adequately explored in the past, is to define hydrocarbon reactivity in terms of the incremental effects of the addition of the hydrocarbon to an already polluted air mass. This appears to us to be a realistic approach to employ when one is concerned with control strategies for hydrocarbon emissions into already polluted areas, such as the California South Coast Air Basin, and thus was the approach this program was designed to investigate.

The major effort on this program was to develop an experimental procedure to measure incremental reactivities, and to test it using several representative organics whose major atmospheric photooxidation reactions are at least moderately well understood. Thus, a simplified 4-component "mini-surrogate" mixture, designed to represent the major features of the complex mixture of organics present in polluted urban atmospheres was developed, and was found to give acceptable agreement, in terms of the major reactivity parameters such as O_3 yields and NO oxidation rates, with a more complex 13-part surrogate mixture designed to represent the distribution of organics emitted in the South Coast Air Basin (Pitts et al. 1976c,d, 1980). Repetitive NO_x -air irradiations of this simplified surrogate were found to give sufficiently reproducible results for these data to be used as a basis for studying the effects of adding varying amounts of test organics.

This surrogate was then employed (a) to determine the effects of incremental additions of toluene in dual-mode outdoor chamber experiments (where the standard mini-surrogate- NO_x mixture and the same mixture with added toluene were simultaneously irradiated on each side of a large, divided Teflon-bag) and (b) to determine the increased effects of addition (or in some cases removal) of toluene, benzaldehyde, propene, n-butane, trans-2-butene, methanol, ethanol, and t-butyl methyl ether in consecutive single-mode indoor chamber irradiations, in which the standard mini-surrogate- NO_x run was alternated with runs with added or removed test organics. The dual-mode approach was judged to be more precise because the irradiation of the control and the test mixtures could be conducted at the same time under the same experimental conditions. However, it was concluded that the single-mode approach was more appropriate for routine use since it (a) was found (at least for toluene) to give results which are consistent with results of dual-mode experiments, (b) was easier experimentally and less costly to employ, and (c) could be done under more reproducible conditions than outdoor dual-mode experiments, allowing for more reliable inter-compound comparisons.

Although there are difficulties in precisely measuring incremental reactivity values for relatively unreactive compounds such as methanol, in general we can conclude that the experimental technique employed in this program can be used to successfully measure incremental reactivity

effects. For a majority of the compounds studied in this program, incremental reactivities defined in terms of O_3 maximum yields and NO oxidation rates were measured with sufficient precision to allow meaningful comparison with theoretical values derived from computer model calculations, and the agreement was sufficiently good to indicate that there are no significant experimental problems or artifacts. For the most reactive compounds, such as benzaldehyde, trans-2-butene, and propene, the effects were large enough so that the dependence of measured incremental reactivities (i.e., $\Delta[\text{reactivity}]/\Delta[\text{organic}]$) on amounts of test compound added to the mini-surrogate ($\Delta[\text{organic}]$) could be determined, and the results were also reasonably consistent with the model calculations. For the less reactive compounds, such as methanol, ethanol, TBME, and n-butane, the dependence of the incremental reactivity on amount of test compound added in the experiments could not be determined with any precision. However, for these compounds, the model calculations indicated that this dependence is small, which suggests that (at least for these compounds) experiments in which sufficiently large amounts of test compound are added to allow a measureable effect to be observed will probably give reasonable estimates of the incremental reactivity values expected when only small amounts of the compound are added.

The experiments conducted in this program allow a ranking of the reactivities of the eight organics studied to be made. However, the data obtained clearly indicate that the rankings would differ depending on how reactivity is defined. In addition, the data indicate that some compounds, including those which are quite reactive when irradiated by themselves in NO_x -air mixtures, exhibit negative reactivity in terms of maximum O_3 yields. Benzaldehyde exhibited by far the largest negative reactivity by all measurements, being the only compound we studied which was unambiguously negatively reactive in terms of NO oxidation rates as well as O_3 yields. This is not unexpected, since benzaldehyde is known to be an efficient radical inhibitor. However, toluene was the next most negatively reactive of the compounds studied in terms of O_3 yields, and propene and trans-2-butene were either slightly negative or slightly positive. All three of these compounds were highly reactive in terms of O_3 formation when irradiated in single hydrocarbon- NO_x -air mixtures (see, for example, Pitts et al. 1979), and had positive incremental reactivity when

defined in terms of NO oxidation rates. Indeed, the alkenes had the highest measured and calculated incremental reactivities relative to NO oxidation rates of all the compounds studied. The remaining compounds studied exhibited positive incremental reactivities both in terms of O₃ yields and NO oxidation rates, with the ordering of the reactivities being approximately what one would expect based on the rates of their reactions with OH radicals.

As indicated above, the observed incremental reactivities, including the "negative" reactivity effects discussed above, are reasonably consistent with results of model calculations, which means that these effects can be accounted for in terms of our current understanding of the atmospheric transformation mechanisms of the compounds studied. In particular, the low or negative incremental reactivity, with respect to maximum O₃ yields, observed for compounds which are highly reactive by themselves and which have positive incremental reactivity relative to NO oxidation rates can be explained by the presence of significant NO_x-removal pathways in the photooxidation of these compounds. This causes O₃ formation to cease (due to lack of NO_x) earlier than would be the case if the compound were not present in the mixture. For toluene, this effect was large enough to more than counter its inducing more rapid O₃ production when NO_x is present. For the alkenes, the two opposing effects tend to cancel each other, causing relatively small net effects on O₃ yields, despite their relatively high rates of reaction in NO_x-air systems.

Another general conclusion which can be drawn from the results of this study is that, for most compounds, the effect on final O₃ yields of adding organics to NO_x-air mixtures which already contain other organics (i.e., already polluted urban atmospheres) is relatively small. For example, the addition of test compounds to increase the total ppmC of organics present in the mixture by 25% caused, in all cases except for benzaldehyde (which as indicated above had a very large and negative effect), less than a 10% change in the maximum O₃. This is consistent with most EKMA-type analyses (e.g., Singh et al. 1981, Carter et al. 1982b, and references therein), which predict that large percentage reductions in hydrocarbons are required to significantly reduce O₃ levels.

The implication of the results of this study in terms of deriving reactivity scales for control and planning purposes are unfortunately difficult to assess. The existence of compounds, such as benzaldehyde, which tend to suppress all aspects of photochemical smog related to O_3 formation and transformation rates has been recognized for some time (Gitchell et al. 1974), and obviously control decisions regarding such compounds must be made based on other criteria, such as potential formation of toxic products or enhanced aerosol formation. The situation is less obvious, however, for compounds which are highly reactive by most measurements but which tend to suppress, or at least not significantly enhance, O_3 yields when added to already polluted mixtures. Even if one is concerned only with ozone levels, and neglects other important considerations such as formation of toxic products or aerosols, it does not appear to us to be advisable to consider compounds such as toluene to be less reactive than compounds such as ethanol or n-butane, simply on the basis of its incremental effects on O_3 levels. In particular, under conditions where NO_x is in excess, which was not the case for the experiments reported here, the tendency of toluene to remove NO_x from the system, which causes reduced O_3 levels in NO_x -poor systems, will not be important, and maximum ozone levels will be more strongly influenced by the rate at which O_3 is formed. Thus toluene would be expected to have positive incremental reactivity under these conditions.

Perhaps the most important conclusion that can be drawn from this study is that even if one is concerned only with O_3 formation, it is a gross over-simplification to attempt to define a single reactivity scale for organics where a given order of ranking represents the O_3 -forming potential of a compound under all conditions. Thus further research in this direction would probably not be useful. A more profitable approach would be to derive multi-parameter reactivity scales, where each parameter represents a different aspect of the atmospheric chemistry of the various organics (such as overall reaction rates, tendencies to suppress or enhance radical and NO_x levels, NO oxidation efficiencies, etc.). Coupled to this would be the development of techniques, probably based on computer modeling, to use these parameters to calculate the effects of increasing or regulating emissions of organics under the conditions of the specific source and receptor areas.

This obviously will be a difficult approach to implement, since it requires a fairly complete knowledge of the levels of reactive compounds present in the source area, as well as an extensive research program concerning the various reactivity characteristics of organics, and how best to measure them and employ them in control strategy calculations. However, progress is being made in this regard as our knowledge of the atmospheric photooxidation mechanisms of a wide range of classes of organics improves and as the identities and levels of the species present in our polluted air basins are more completely characterized. Also, progress continues in the development of more reliable and sophisticated techniques to model the transformations occurring in those air basins.

Realistically, however, it will be a number of years before reliable techniques are developed to derive hydrocarbon reactivity scales appropriate for the various source areas of concern, and until such techniques are available, existing hydrocarbon reactivity scales should be used only with great caution when making emission control strategy decisions.

VI. REFERENCES

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